

ELECTROLYTIC PREPARATIONS

**EXERCISES FOR USE IN THE LABORATORY BY
CHEMISTS AND ELECTRO-CHEMISTS**

BY

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TRANSLATOR'S PREFACE

THE great advances made during recent years in the applications of electro-chemistry, which have led to the development of important industries, have also given us simple and efficient processes suitable for the preparation in the laboratory of a large number of useful chemical substances. So few works dealing with this subject are available that the writer hopes to be contributing to the more extended adoption of electrolytic preparations in the laboratory, by presenting an English translation of a book which he has already found to be of great service for instruction in this subject. He is greatly indebted to his friend Dr. A. T. de Mouilpied for many kind suggestions, and for reading through the proof sheets of the translation.

AUTHOR'S PREFACE

A LARGE number of works are available for the education of students in preparations of a purely chemical nature. In the numerous recent introductions to practical electro-chemistry, although the physical side of the teaching of the electro-chemist is fully dealt with, the chemical preparative portion is usually little developed. The importance of this branch of the subject is, however, already sufficiently great, and it does not seem to me at all superfluous to publish a small collection of exercises, which are exclusively chosen from those made use of for introducing the students at the Giessen electro-chemical laboratory to the chemical preparative side of electro-chemistry. It is presupposed that those who intend to make use of these exercises have already followed a course of inorganic and organic preparations, and in practical physics have acquired the necessary knowledge, particularly of the laws of the electric current, as also of electrical measuring instruments and methods of performing measurements; and finally have carried out simple electro-chemical exercises, such as the determination of the capacity of an accumulator, its efficiency in ampere hours and watt hours, the determination of the influence of current density and concentration of the electrolyte, in simple cases of electrolysis.

With a view to the improvement of this small work, I shall always be thankful for suggestions from my colleagues.

K. ELBS.

GIESSEN,

Autumn, 1901.

NOTES ON REFERENCES AND ABBREVIATIONS

THE references given at the headings of the different exercises, although numerous, are not to be considered as exhaustive: in the case of those subjects which have been somewhat fully investigated, only a few selected references are given.

Such papers as are considered to be of chief importance for the purposes of the particular experiment are denoted by an asterisk.

For a complete survey of the literature of the subject the use of the *Jahrbuch der Elektrochemie* is to be recommended. The volumes 1-8 deal with the progress during the years 1894-1901.

[For English readers fairly complete abstracts of the different papers may frequently be found in the Journals of the Chemical Society or Society of Chemical Industry, and nearly all the important German patents are duplicated in the publications of the British and U. S. A. Patent Offices.—TR.]

The following abbreviations have been adopted for the references :

<i>A.</i>	= <i>Liebig's Annalen der Chemie.</i>
<i>B.</i>	= <i>Berichte der Deutschen Chemischen Gesellschaft.</i>
<i>C.</i>	= <i>Chemisches Centralblatt.</i>
<i>Compt. rend.</i>	= <i>Comptes rendus des Séances de l'Académie des Sciences.</i>
<i>Ch. Ztg.</i>	= <i>Chemiker-Zeitung.</i>
<i>Chem. Soc.</i>	= <i>Journal of the Chemical Society (London).</i>
<i>Amer. Chem. Soc.</i>	= <i>Journal of the American Chemical Society.</i>
<i>J. S. C. I.</i>	= <i>Journal of the Society of Chemical Industry.</i>
<i>J. pr.</i>	= <i>Journal für praktische Chemie.</i>
<i>Z. ang. Ch.</i>	= <i>Zeitschrift für angewandte Chemie.</i>
<i>Z. anorg. Chem.</i>	= <i>Zeitschrift für anorganische Chemie.</i>
<i>Z. Elch.</i>	= <i>Zeitschrift für Elektrochemie.</i>
<i>Z. ph. Ch.</i>	= <i>Zeitschrift für physikalische Chemie.</i>
<i>D. R. P.</i>	= <i>Deutsches Reichs-Patent.</i>

Abbreviations in text :

D_A = Current density at the anode.

D_C = Current density at the cathode.

CONTENTS

PART I. GENERAL

	PAGE
I. SOURCE OF CURRENT AND CONNEXIONS	1
II. RESISTANCES	3
III. MEASURING APPARATUS AND MEASUREMENTS	4
IV. APPARATUS FOR ELECTROLYSIS	10

PART II. SPECIAL

I. EXAMPLES FROM INORGANIC CHEMISTRY

A. EXPERIMENTS WITH UNATTACKABLE ANODES	17
1. Oxidation of Chromium Sulphate to Chromic Acid	17
2. Preparation of Sodium Hypochlorite	21

Chlorates, Bromates, and Iodates.

3. Potassium Chlorate from Potassium Chloride	26
4. Sodium Chlorate from Sodium Chloride	27
5. Potassium Bromate from Potassium Bromide	28
6. Sodium Bromate from Sodium Bromide	28
7. Potassium Iodate from Potassium Iodide	29

Perchlorates.

8. Potassium Perchlorate from Potassium Chlorate	33
9. Preparation of Ammonium Persulphate from Ammonium Sulphate	35

B. EXPERIMENTS WITH SOLUBLE ANODES	40
10. Cuprous and Cupric Oxides from Copper	40
11. White Lead from Metallic Lead	41
12. Lead Disulphate (Plumbic Sulphate) from Metallic Lead	42
13. Production of pure Copper from Brass	45

II. EXAMPLES FROM ORGANIC CHEMISTRY

	PAGE
A. ELECTROLYSIS OF ORGANIC ACIDS	47
14. Ethane from Sodium Acetate	51
15. Ethylene (Ethylene Dibromide) from Sodium Propionate	53
16. Trichlormethyl Ester of Trichloroacetic Acid from a mixture of Sodium and Zinc Salts of Trichloroacetic Acid	54
17. The Ethyl Ester of Adipic Acid from the Potassium Salt of the Ethyl Ester of Succinic Acid	56
B. ELECTRO-CHEMICAL METHODS OF REDUCTION	57
I. Electro-chemical Reduction of Aromatic Nitro-compounds	57
i. <i>Reduction in moderately Acid Solution; preparation of Amines</i>	68
18. Aniline from Nitrobenzene	68
ii. <i>Reduction in strong Acid Solutions; preparation of Hydroxylamine Derivatives</i>	69
19. <i>p</i> -Amidophenol from Nitrobenzene	69
20. <i>p</i> -Amidophenolsulphonic Acid from Nitrobenzene	71
21. Benzylidene Phenylhydroxylamine from Nitrobenzene and Benzaldehyde	72
iii. <i>Reduction in Alkaline Solution; preparation of Compounds and Derivatives of the Azo and Amine Series</i>	73
1. <i>Azoxy Compounds.</i>	
22. Azoxy- <i>m</i> -xylene from Nitro- <i>m</i> -xylene	74
23. <i>m</i> -Dichlorazoxybenzene from <i>m</i> -Chloronitrobenzene	75
24. <i>p</i> -Azoxyanisole from <i>p</i> -Nitroanisole	76
25. Azoxybenzene from Nitrobenzene	76
2. <i>Azo Compounds.</i>	
26. Azobenzene from Nitrobenzene	78
27. <i>m</i> -Azobenzoic Acid from <i>m</i> -Nitrobenzoic Acid	79
28. <i>m</i> -Diamidoazobenzene from <i>m</i> -Nitraniline	80
3. <i>Hydrazo Compounds and Benzidines.</i>	
29. Hydrazobenzene and Benzidine from Nitrobenzene	82
30. <i>m</i> -Diamidohydrazobenzene and <i>m</i> -Diamidobenzidine from <i>m</i> -Nitraniline	83
31. Benzidine- <i>m</i> -disulphonic Acid from <i>m</i> -Nitrobenzenesulphonic Acid	85

4. *Diamines and Amidophenols.*

	PAGE
32. <i>p</i> -Phenylenediamine from <i>p</i> -Nitriline	87
33. <i>p</i> -Amidophenol from <i>p</i> -Nitrophenol	88
II. Electro-chemical Reduction of Carbonyl Compounds	89
34. Preparation of Phenyl- <i>p</i> -tolylpinacone from Phenyl- <i>p</i> -tolyl- ketone	91
35. Benzhydrol from Benzophenone	92
36. Deoxycaffeine from Caffeine	93
C. ELECTRO-CHEMICAL OXIDATION METHODS	94
37. Preparation of Iodoform	94
38. <i>p</i> -Nitrobenzylalcohol from <i>p</i> -Nitrotoluene	96

APPENDIX

Table of Atomic Weights and Electro-chemical Equivalents	98
INDEX.	99

PART I. GENERAL

I. SOURCE OF CURRENT AND CONNEXIONS

ACCUMULATORS alone come into consideration as a source of current for preparative work in the laboratory. To carry out the experiments detailed in the special part of this book, potentials above 18 volts are never required, and consequently nine cells with a voltage of $2 \times 9 = 18$ v. are sufficient, whilst most requirements would be fulfilled by a battery of only five cells.

The preparations can all be carried out with currents of one to two amperes; in order, however, to be able to work quickly, and on a somewhat larger scale, it is convenient to have at one's disposal currents up to 25 amperes. The capacity of the accumulator-cells is to be chosen according to these requirements.

For the sake of convenience several connexions are made from the battery of accumulators, arranged in series, to the working places, so that different voltages in suitable steps are available. For instance, a four-wire connexion from a nine-cell battery gives potentials of 4 v., 6 v., 8 v., 10 v., 14 v., and 18 v. at the four terminals on the working benches, as is shown in Fig. 1; a three-wire connexion from a five-cell battery, potentials of 4 v., 6 v., and 10 v.

With such an arrangement a small adjustable resistance is sufficient for the requirements of the experiments; in fact, one can frequently work without any such resistance. The dimensions of the connexions must be liberally chosen, so that only a small loss of voltage occurs in the leads; the rate being one thousand amperes per sq. in. cross-section of copper. To simplify the moving of the apparatus, flexible cords instead of ordinary copper wire are to be

recommended for currents up to three amperes; for larger currents, well-covered thin copper wire should be used. On both ends of these temporary connexions short lengths of thick copper wire should be soldered, as these are not only more convenient for fixing to the terminals, but also considerably more lasting. Uncovered wire is unsuitable for leads from the terminals to the apparatus on account of the danger of short circuiting.

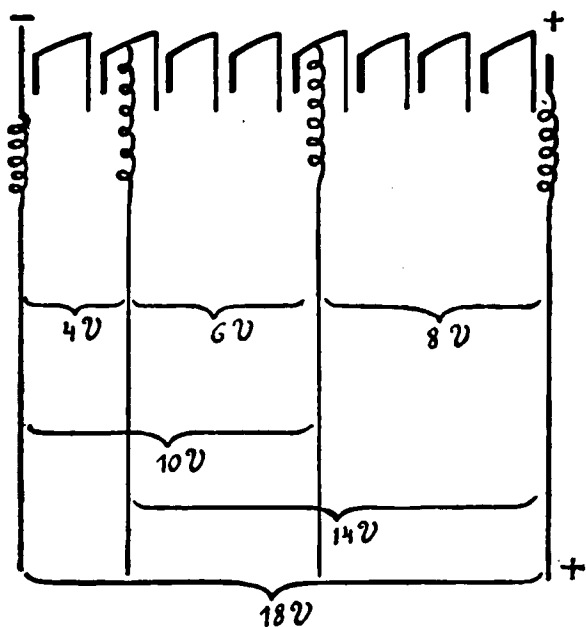


FIG. 1.

If the permanent leads are provided with fuses, as is to be always strongly advised, separate fuses for the individual experiments are unnecessary. In most cases, special switches and keys can be dispensed with, the fixing or removal of a wire in the terminal sufficiently fulfilling the purpose.

The terminals should be large, strong, and provided with wide bore; they must, of course, be kept quite clean, although a brightly polished surface is not essential. This is easily accomplished by brushing them occasionally under

a water-tap, after which they are dried and soaked in paraffin oil: the film of paraffin oil which remains, protects them well against corrosion, without perceptibly increasing the resistance for the current. Some three-way connectors are necessary; as, for instance, when the potential difference in an electrolytic cell has to be measured; in this case both anode and cathode carry a three-way connector, of which one terminal is connected to the electrode, another to the main current, whilst the third is used for the voltmeter wire.

When in doubt as to which is the + or — lead, it is only necessary to press the ends of both leads on to a moistened piece of reagent paper¹; the negative pole produces a purple red spot.

II. RESISTANCES

For regulating the strength of current, resistances of nickeline wire (Rheotan wire) of 1.50 to 1.75 mm. diameter are employed; these will carry 20 to 25 amperes, as shown by the following table:—

NICKELINE WIRE².

Diameter in mm.	Cross-section in square mm.	Resistance in ohms of 1 m. length.	Limiting allow- able current in amperes.
0.5	0.196	2.00	4
1.0	0.785	0.51	10
1.5	1.767	0.23	23
2.0	3.141	0.13	39

¹ Preparation of Pole Reagent paper. A half-saturated, aqueous solution of common salt is mixed with a very small quantity of phenolphthaleïn dissolved in excess of alcohol; filter-paper is soaked in the well-stirred mixture and then dried. The negative pole is indicated on a moistened piece of this paper on which the two wires are placed, by the red colouration caused by the formation of sodium phenolphthaleïn by alkaline reaction.

² Resistance Wire. Similar data for the better known materials, such as Manganin, Platinoid, German Silver and Eureka can be found in most textbooks on Electricity.—Tr.

If terminals with conveniently arranged voltages, as described above, have been provided, a total regulating resistance of only 0.5 to 1 ohm will be required; that is, three to five metres of such wire. The usual form of regulating resistance only admits of decreasing the resistance step by step and thus the strength of current—a disadvantage, however, which is not of consequence in most of the preparations; on the other hand, resistances with sliding contact allow the continuous variation of the resistance and thus the adjustment of the current to any fixed value, and are in consequence useful for all cases. Very often the use of a regulating resistance is altogether unnecessary if voltages in suitable gradations are provided; in this case it is only necessary, as soon as the current has sunk below the minimum allowable, to change over to the next higher voltage, whilst if it has risen too high, the next lower voltage is employed—a method which is very convenient, as is shown by Exercise No. 22.

Regulating resistances remain in good condition, despite the vapours of the laboratory, if they are often rubbed over with a cloth soaked in paraffin oil. Liquid resistances are unnecessary for preparative work.

III. MEASURING APPARATUS AND MEASUREMENTS

For the electrolytic preparations, measurements of the following values are required:—

1. Current strength by means of an ammeter, or voltmeter and chronometer.
2. Amount of electricity (coulombs) by means of an ampere-hour meter.
3. Potential difference at the cell and polarization by means of a voltmeter.

1. For the measurement of the current strength, the small forms of the usual technical ammeters are all that is

required. The more accurate instruments are unsuitable for use in the corrosive atmosphere of a chemical laboratory, and should be used only to calibrate the cheaper instruments from time to time to denote the errors in the latter, which corrections should be employed in their everyday use. Dead-beat instruments are not required. Incomplete damping is not of much consequence, since generally there is quite sufficient time for the pointer to come to rest. Of greater importance is the low resistance of the instruments, so that, since they remain in circuit during the whole experiment, they shall not cause a considerable drop in voltage and become too much heated by the passage of the currents they are made to measure. Water and copper voltameters will only be employed to measure the strength of current in particular cases, the former for instance in electrolytic reductions, in which case the volumes of the gases from the voltameter and from the experimental cell can at any time easily be compared, and thus the progress of the reaction at once observed.

The only water voltameter we need consider is the alkaline form due to Oettel, in which 15 per cent. sodium hydrate (free from chloride) is electrolysed between nickel electrodes. Two cylindrically bent nickel electrodes are placed in caustic soda solution in a glass cylinder, which is provided with a rubber stopper; through this two thick nickel wires, serving as connexions, and a glass tube for leading off the gases, pass air-tight; the nickel wires are preferably riveted to the electrodes. The ampere-manometer of Bredig and Hahn¹ can be used as an Oettel voltameter, if the capillary tube (Fig. 2) is replaced by an ordinary gas-delivery tube. From the observations the mean current strength as measured by the water voltameter can be calculated by the formula:

$$I_A = \frac{v(b-12)}{760(1+0.00366t) \times 10.44z},$$

¹ *Z. Elch.* 7, 259 (1900).

where I_A is the current strength in amperes, v the volume of gas evolved, b the height of the barometer in millimetres of mercury, t the temperature in degrees centigrade, and z the time in minutes during which the gas has collected.

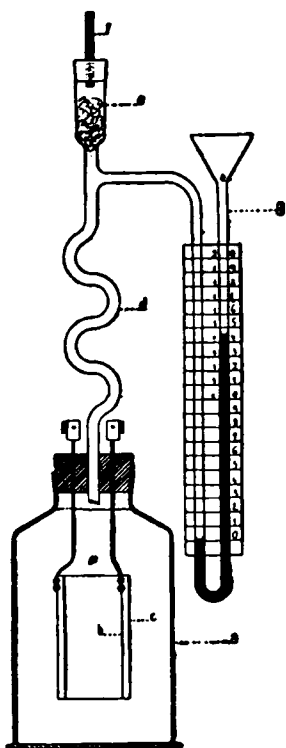


FIG. 2.

In the copper voltameter, acidified copper-sulphate solution is electrolysed between copper electrodes. Three rectangular copper sheets are employed, at least 3 mm. thick, and each provided with two long lugs at one end; these plates are hung parallel to one another in a rectangular glass vessel, so that the lugs, which also serve for connecting to the source of current, rest upon the edge of the vessel; by inserting glass rods between the plates, short circuiting is prevented. The middle sheet is used as a cathode, the two exterior ones as anode; but from time to time in later experiments one of the anode plates replaces the cathode, so that one is not continually getting thinner whilst the other gets thicker. The sheets should be at least 3 cms.

from the bottom of the vessel. The following solution recommended by Oettel¹ should be used as electrolyte:

150 gms. cryst. Copper sulphate,
 50 gms. Sulphuric acid,
 50 gms. Alcohol,
 1000 gms. Water.

For experiments of long duration, an occasional stirring of the solution with a glass rod is not sufficient, but provision must be made for a continual mixing of the electro-

¹ *Ch. Ztg.* 17, 543 (1893).

lyte, as, for instance, by means of a moderate current of hydrogen gas. After the experiment the cathode is removed, washed first with water, then with alcohol, and dried quickly over a flame. For weighing a sensitive analytical balance is unnecessary. The mean current strength during an experiment is calculated from the formula :

$$I_A = \frac{N}{0.0198 z},$$

where I_A is the current strength in amperes, z the duration of the experiment in minutes, and N the weight of deposited copper in grams. The measurement can, moreover, only be made by determining the increase of weight of the cathode, not by determination of loss of weight of the anodes, since the latter is indefinite. The copper voltameter, under the conditions described, gives accurate values with current densities of 0.06 to 1.5 amperes per 100 sq. cms. cathode surface, and, with good circulation of the electrolyte, even up to 2.5 amperes per 100 sq. cms. The copper-sulphate solution alters its composition only slightly, and can be employed for a considerable time.

2. For the measurement of the amount of electricity which has passed through the electrolytic bath during an experiment, the Oettel copper voltameter just described is most suitable as an ampere-hour meter. We have

$$M_{A.H.} = \frac{N}{1.184},$$

where $M_{A.H.}$ is the amount of electricity in ampere hours, and N the deposit of copper in grams. With experiments of long duration, or such as cannot be uninterruptedly observed, as also with those in which sudden and considerable fluctuations in the current occur, an ampere-hour meter should always be included in the circuit. In other cases this can be dispensed with, since from readings of the current and time the ampere hours can be easily calculated.

3. The measurement of the potential difference and the polarization of an electrolytic cell by means of a voltmeter demands conditions from such an instrument which the cheaper forms are often unable to satisfy, because their resistance is too small and the damping insufficient. A voltmeter connected with the electrodes during the passage of the current gives the potential difference of the electrolytic bath; this depends on the strength of current, the resistance of the bath, and the polarization of the electrodes. Since the voltmeter is placed as a shunt by this measurement, the amount of the total current, as measured by the ammeter, which passes through the voltmeter does not pass through the bath; if therefore the resistance of the voltmeter is small, this shunt-current is large, and a noticeable error is introduced, if it be not subtracted from the current strength and the amount of electricity which has been supplied to the bath. The voltmeter must, therefore, possess a considerable resistance, at least 30 to 40 ohms¹; it is of course not connected, as is an ammeter, during the whole of the experiment, but from time to time is connected with the electrode terminals in order to read off the potential difference of the bath. The polarization can be determined with sufficient accuracy by breaking the main circuit whilst the voltmeter is connected with the electrodes. The voltmeter, which had previously shown the potential difference of the bath, falls, remaining for a short time at some fixed point—this point of the scale gives the polarization voltage—and then falls more or less slowly back to the zero. The substances covering the electrodes which cause the polarization are used up by the polarization current in accordance with Faraday's law; moreover, the voltmeter does not directly show the electromotive force of the polarization—the electrode potential—but rather the terminal voltage of the polarization current. For both reasons, the necessity of employing a voltmeter of high resistance and good damping is obvious; for, if the polarization current is

¹ 30-40 ohms per volt.—Tr.

only very weak, the terminal voltage read can with sufficient approximation be taken equal to the electromotive force of the polarization, and with good damping there is sufficient time to read the voltage, which remains constant some instants. If the resistance of the voltmeter is known, the current in amperes can be calculated from the reading in volts, and if at short intervals time and current strength are noted, important conclusions as to the nature and amount of the polarizing substances can often be obtained from the polarization discharge thus observed.

Whereas the potential difference of the bath and also generally the polarization are easily determined, the measurement of the single potentials of anode and cathode requires sensitive apparatus, with which measurements are difficult to carry out with the ordinary baths. From a theoretical point of view, for most of the reactions which take place at the electrodes, the potential of the electrode is indeed all-important; practically, however, this constant has by no means the importance which is ascribed to it. Firstly, its value is often considerably altered by minute alterations in the conditions; moreover, it is difficult to obtain the larger currents which are necessary for preparative methods, at the same time keeping a fixed potential at the electrode; whilst finally, other influences and experimental conditions often have more importance than the action of a given electrode potential. Under otherwise similar conditions, current density (current strength in amperes, to the unit surface) and electrode potential are closely connected; for, although they do not stand in direct proportion, the electrode potential rises with increasing current density and conversely. In general, for preparative work, the knowledge of the current density suffices, especially since reactions which are connected with a narrowly limited electrode potential, can only exceptionally be employed in a practical preparative method. Moreover, the statement of the current density is often sufficient to re-establish any given electrode potential conditions. In the

description of an experiment the statement of the current density is thus indispensable, and it is very fortunate that for its determination no special measurement is necessary, since the dimensions of the electrode and the current strength would in any case need to be known.

IV. APPARATUS FOR ELECTROLYSIS

Electrolytic cells should be fitted up as simply as the purposes of the experiment render possible; examples of how this can be accomplished in individual cases will be given in the special part of this book. The great advantages of glass on account of its insulation, non-corrosiveness, and transparency, lead to the almost exclusive employment of beaker glasses and rectangular glass cells for electrochemical laboratory experiments; these can be obtained in the most varied sizes. In many electrolyses which have to be carried out at a higher temperature, there is no need to heat the bath externally, for, if the solutions are previously heated and the electrolysis carried out with high concentration of current¹, the heating effect of the current is in a short time sufficient for the realization and maintenance of the required temperature. A constant and rapid removal of the electrolyte in the immediate neighbourhood of the electrode is frequently necessary for the favourable progress of the reaction. This is most readily accomplished by a mechanical stirring arrangement; but the apparatus is often inconveniently complicated in this way, and indeed, in the larger number of cases, the result can be accomplished by a suitable arrangement of the experiment without the use of any special stirring apparatus. Mechanical stirrers can generally be replaced in the small-scale experiments by the use of wire-gauze or perforated metal as electrodes, by employment of the

¹ Concentration of current = $\frac{\text{current strength}}{\text{volume of electrolyte}}$ is a convenient expression introduced by Tafel, *Ber.* 33, 2209 (1900).

electrolyte in a thin layer, or circulation of the solutions by the evolution of gas or vapour bubbles within them, by one-sided heating, or by production of different density in different portions of the liquid, or by similar methods.

The electrodes form the most important part of a bath, and upon their correct selection and condition the success of an electrolysis depends above all. Expensive platinum electrodes and inconvenient mercury electrodes are only made use of when they cannot otherwise be avoided. For cathodes the choice of materials is considerable, since almost all the ordinary metals in weak acid, neutral, or weak alkaline solutions can be considered as unattackable cathodes, for even in such liquids as are capable of attacking these metals, the cathode is protected during the passage of the current. In strong acid solutions, copper, and often nickel or lead, are suitable; whilst in strongly alkaline liquids copper, nickel, and iron are employed as cathode metals.

As material for unattackable anodes, however, only platinum (platinum-iridium), carbon, lead, nickel, and iron come into consideration. Platinum can be employed under all conditions in acid and alkaline electrolytes, as it is not perceptibly attacked even by free chlorine. Carbon is only suitable if the solutions are acid or neutral, and when no oxygen evolution occurs at the anode, otherwise even the best retort graphite is quickly disintegrated. Lead is available in all cases where it becomes coated with a strongly adherent coating of lead superoxide, this is the case in free sulphuric acid up to specific gravity of 1.6, in phosphoric acid of any concentration, also in aqueous acid or neutral solutions of sulphates, phosphates, carbonates, or chromates; in the latter, however, only with safety when they also contain sulphates. Nickel anodes are permanent in alkalis and alkaline carbonates (in absence of ammonia). This does not hold unconditionally with iron, since ferrites and ferrates can be formed; iron, however, can be used in sulphuric acid above 1.7 sp. gr., and in nitric acid above 1.3 sp. gr.

Except in those cases where a high current density is required, the electrodes are chosen as large as possible, in order to decrease the resistance of the bath. In this connexion it should be pointed out that, in preparative experiments in the laboratory, the voltage required usually depends much more on the resistance of the bath than on the polarization, and consequently there is no saving in the electrical energy in working with a small amount of substance in a small apparatus. For if one employs four times the weight of substance in an apparatus four times as large, although four times the quantity of electricity is required, yet, since the larger apparatus only needs about a quarter of the bath-voltage of the smaller, the expenditure of energy is approximately the same in both cases. Without doubt the observations are easier and more trustworthy, and the working up of the products is more simple and sure with a reasonable amount of substance than with very small quantities amounting only to a few grams.

As a matter of principle one should strive to involve the smallest expenditure of electrical energy; in this way unnecessarily high current densities are avoided, and if in an experiment there is a choice between several kinds of electrolytes or different concentrations, that possessing the smallest resistance should be chosen. In all cases where it is advantageous to have a rapid renewal of the electrolyte in the immediate neighbourhood of the electrode, perforated metal or gauze electrodes should be employed in preference to massive plates. Very troublesome is the fact that even those electrodes which are not appreciably attacked chemically, gradually show a mechanical disintegration, especially with high current densities, resulting in the dissipation of their material, roughening of their surface, and ruin of their structure. In consequence of this behaviour, the employment of very fine wire-gauze or very thin platinum foil, despite the saving in weight, is often most unsuitable; as an instance, the electrodes of

very thin platinum foil¹, which are otherwise so convenient, become very brittle after short use.

For current connexions platinum wires of sufficient thickness and length are welded to platinum electrodes—a platinum wire of 0.5 sq. mm. cross-section should at the most carry 1.5 amperes, one of 1 sq. mm. a current of 2.5 amperes—and to the end of the platinum wire a copper wire should be soldered, so that the platinum is not broken off by the connector-screws. Carbon electrodes either have terminals such as are used in galvanic batteries, or the

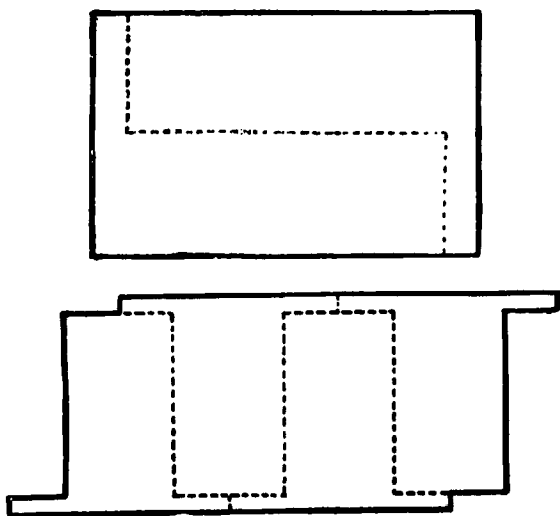


FIG. 3.

upper end is electrolytically coppered and a copper wire soldered to this deposit. Electrodes of ordinary metals, either sheet or gauze, are cut with a projecting lug, on which either a copper wire is soldered or a connector fixed. These lugs must be sufficiently long so that neither the solder nor connector comes in contact with the electrolyte; the copper wire, especially with gauze electrodes, must be soldered over a good length. Fig. 3 shows how electrodes can be cut for this purpose with as little waste

¹ Heraeus, *Z. Elch.* 7, 671 (1901); *Electrician* 47, 911 (1901).

as possible. Lead anodes, on which a thick layer of lead peroxide, mixed with sulphate, phosphate, carbonate, or chromate, has been deposited, conduct very badly; this trouble can be overcome by dipping the electrodes for a short time in very dilute nitric acid to which a little sodium nitrite solution has been added, and then brushing off the deposit under a water-tap. In experiments which require a fixed and abnormally low cathode potential, as for instance the reduction of caffeine, a contamination of the cathode by less electro-positive metals must be carefully avoided. This is accomplished, with lead cathodes, by a simple method, which is described in the special part of the book in connexion with the reduction of carbonyl compounds.

Except where otherwise stated, the measurements given for electrodes refer to the single surface; even with gauze and perforated electrodes, calculations are made on the measurement of one side, which, if one side alone is used, corresponds approximately with the actual conditions.

Heating or cooling of the bath is frequently necessary; this can often be very conveniently and effectively accomplished by employing one of the electrodes in the form of a spirally wound tube which is used for cooling circulation or for steam.

Most of the electro-chemical methods of preparation require a separation of the anode and cathode liquids by means of porous partitions in the cell. All the diaphragms which are available at the present time are imperfect, and therefore any method which does not require a diaphragm possesses great advantages. In moderately acid solutions, animal membrane or parchment paper can be used as a porous separation medium; porous cells are more permanent, and these can be had of almost any shape, but of very varying perfection.

In strongly acid solutions only porous cells, in alkaline solutions porous cells and cotton cloth can be employed; under some conditions asbestos with parchment or cloth may

find application in laboratory experiments¹. For the satisfactory preservation of porous cells it is most necessary to rinse them out immediately after use, and then keep them in a large vessel full of water; no part of the cell should emerge from the water, which must be frequently renewed. Thick and dense cotton cloth, which is to be used as a diaphragm, must first be well washed out and afterwards, whilst still wet, stretched on a glass plate or board; it is

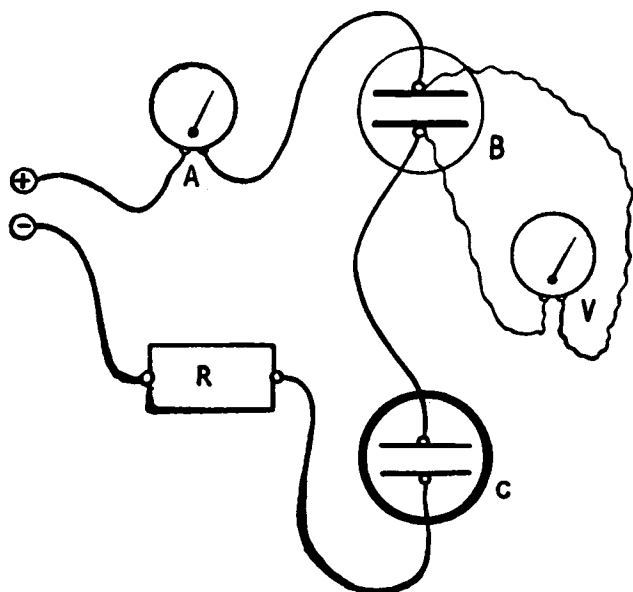


FIG. 4.

then soaked with caustic soda of 1.26 sp. gr.; after 10 to 20 minutes it has reached a leathery consistency and is well washed out whilst still stretched; after use the cloth is preserved under water as recommended for the porous cells.

A complete arrangement for an electrolytic experiment

¹ The excellent Pukall cells (see Häussermann and Fein, *Z. ang. Chem.* 1894, 9) are too expensive for general use; cement diaphragms suitable for alkaline solutions are not available commercially; those recommended by Le Blanc for acids (*Z. Elch.* 7, 653 (1901)) possess many valuable properties.

is shown in Fig. 4 ; it consists, with the exception of the source of current and leads, of the decomposition-cell (bath) B, ammeter A, and voltmeter v, ampere-hour meter C, and regulating resistance R. One can often dispense with the ampere-hour meter and the resistance, and sometimes with the voltmeter ; but however simple the experiment may be, the ammeter must always be retained, even when a voltmeter is in circuit, for the latter only denotes the mean current during any given interval of time, and does not indicate the strength of current at any given instant, nor the variations of current.

PART II. SPECIAL

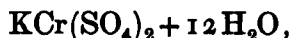
I. EXAMPLES FROM INORGANIC CHEMISTRY

A. EXPERIMENTS WITH UNATTACKABLE ANODES.

I. OXIDATION OF CHROMIUM SULPHATE TO CHROMIC ACID.

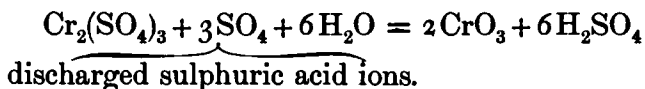
References: Farbwerke vorm. Meister Lucius und Brüning, *Brit. Patent*, No. 15,724, 1898*, *Z. Elch.* 6, 256, Ref., *J. S. C. I.* 18, 685, 1124 (1899), Ref.; F. Regelsberger, *Z. ung. Ch.* 1899, 1123*.

A BEAKER or cylindrical lead vessel contains a porous pot with a lead plate as cathode, in the outer anode portion of the cell a lead cylinder as anode. The anode and cathode liquids consist of a chromium solution prepared in the following manner:—200 grams chrome alum,



are dissolved in hot water, 150 c.c. concentrated sulphuric acid are added, and the solution is made up to 1,000 c.c. The cell is filled with the solution whilst still hot, and is kept in a basin of hot water. The electrolysis is carried out with a current density at the anode $D_A = 2$ to 3 amperes per 100 sq. cm. at a temperature of 40 to 60 degrees. The current efficiency for some time exceeds 90 per cent. of the theoretical, but falls rapidly as soon as a considerable proportion of the chromium salt has been oxidized. The anode becomes covered with a layer of lead peroxide before the regular oxidation of the chromium salt begins; at first the evolution of oxygen is very small, but it increases in proportion as the solution becomes poorer in chromium salt

and richer in chromic acid. In order to carry out the experiment in accordance with the actual conditions, the current density should be continuously decreased in proportion to these variations in concentration. The process is expressed by the equation



At the cathode hydrogen is evolved almost quantitatively, since in the acid solution the H ions are more easily discharged than the Cr^{+++} ions, and moreover the partial discharge of Cr^{+++} ions to Cr^{++} ions (reduction of the chromic to chromous salt) only takes place with difficulty. A small deficiency in the hydrogen can be detected without finding a corresponding amount of chromous salt, which is explained by the property of the chromous salts of being quickly transformed into chromic salts by taking up oxygen from the air.

The separation of the chromic acid from the solution as chromate is inconvenient; the yield can be estimated and the progress of the reaction observed by titrating samples (after well stirring the whole of the solution) with ferrous ammonium sulphate and potassium permanganate, since the titrating back of the excess of Mohr's salt can be effected with sufficient exactness in daylight, despite the strong green colour of the solution. In order to avoid considerable variations in the total amount of solution by the taking of samples, and thus a large error, the experiment is carried out with at least 500 c.c. anode liquid, and the electrolysis stopped so soon as the current yield begins to decrease greatly. As an example, the following tables and curves represent an experiment:—

Anode: Lead cylinder of $30 \times 10 = 300$ sq. cms.

Cathode: Lead plate of $6 \times 10 = 60$ sq. cms.

Electrolyte: Chrome alum solution of composition given above.

Anode liquid: 1,200 c.c.

Current = 6 amperes, kept constant by a regulating resistance.

Duration of experiment : 2 p.m. to 6 p.m. = 4 hours.

Temperature = 52° C.

1 ampere hour yields theoretically 1.25 gms. CrO_3 .

The anode having a bright metallic surface, the oxidation at this electrode is at first employed in producing a layer of lead peroxide, which explains the low current yield in the first half-hour.

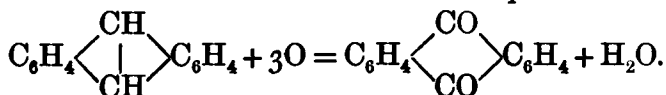
TABLE I.

Time.	Sum of am- pere hours.	Con- tent of CrO_3 in gms.	In- crease of CrO_3 in gms.	Calculated in- crease of CrO_3 in gms.	Current yield in percentage of theoretical.	Remarks.
2						Oxygen Evolution :
2.30	3	2.8	2.8	3.75	74.6	Small.
3	6	6.2	3.4	3.75	90.6	Very small.
3.30	9	9.6	3.6	3.75	96.0	" "
4	12	13.2	3.6	3.75	96.0	" "
4.30	15	16.7	3.5	3.75	93.3	" "
5	18	19.9	3.2	3.75	85.3	Moderate.
5.30	21	22.2	2.3	3.75	61.3	"
6	24	23.0	0.8	3.75	21.3	Considerable.

The mean current yield during four hours amounts to 76.7 per cent.

Fig. 5 shows the graphical representation.

The process of the electrolytic oxidation of chromic salts to chromic acid is of great technical importance. In the colour industry a mixture of potassium or sodium bichromate and sulphuric acid is employed amongst other purposes for the oxidation of anthracene to anthraquinone.



The oxidation mixture after use consists of a solution of potassium or sodium sulphate, chromium sulphate, and sulphuric acid in water, and is always regenerated electrolytically. It is employed as anode and cathode liquid. By the action of the current, chromic acid is produced at the anode, whilst at the cathode hydrogen is evolved. Besides this, an alteration in the concentration of the sulphuric acid takes place; an increase at the anode and decrease at the

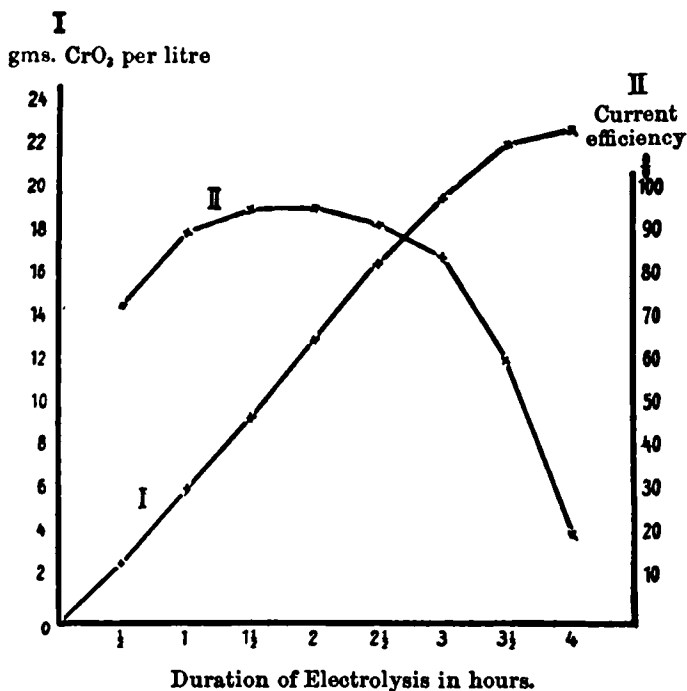


FIG. 5.

cathode. The oxidized liquid from the anode chamber can be directly employed in the manufacturing process, and is thus again transformed into a chromic salt solution; after this, it is placed in the cathode portion of the cell, whilst the first cathode liquid is now employed for the anode. In the second treatment the cathode liquid is at first richer in sulphuric acid than the anode liquid, but by the passage of the current the excess migrates from the former to the

latter. By this arrangement of the cycle, in employing the liquid alternately for cathode and anode, the object of preventing a concentration of the sulphuric acid is attained, and as a matter of fact the same liquid in unaltered composition and without loss of material can be employed for any length of time as an excellent oxygen carrier.

2. PREPARATION OF SODIUM HYPOCHLORITE.

References : F. Oettel, *Z. Elch.* 1, 69, 356-358*, *Ch. Ztg.* 18, 69 (1894); H. Bischoff and F. Foerster, *Z. Elch.* 4, 464-470; A. Sieverts, *Z. Elch.* 6, 364-370*, 374-378*; P. Schoop, *Z. Elch.* 2, 209, 227-231; Hermite, *J. S. C. I.* 6, 170, 246 (1887), *Brit. Patent*, Nos. 13,929 (1884), 14,673 (1886), and later ones; Haas and Oettel, *Brit. Patent*, 1697 (1898), 9331 (1900); Haas, *Brit. Patent*, 10,215 (1899); Stelzer, *German Patent*, No. 111,574; K. Kellner, *German Patent*, No. 104,443; F. Gebauer, *German Patent*, No. 80,617; F. Oettel, *Z. Elch.* 7, 315-320, 449-451; V. Engelhardt, *Z. Elch.* 7, 390-396.

A tall glass vessel, which is cooled with water on the outside, serves as a bath; anode and cathode consist of platinum foil. The anode is suspended vertically on one side of the bath in the upper part of the electrolyte, whilst the cathode is on the opposite side in the lower part; on account of the evolution of the hydrogen at the cathode, a circulation of the electrolyte is effected by this arrangement, which is favourable for the success of the process.

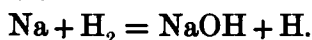
Electrolyte: solution of common salt of a concentration of 3 gram molecules = 175 gms. per litre. $D_A = D_C = 15$ amps. per 100 sq. cms. Current yield at first over 90 per cent., sinking gradually to below 30 per cent.; a concentration of about 14 gms. NaOCl per litre can be attained with fair current yield. Low current density at the cathode diminishes the yield; the same, but to a less marked degree, is true for low current density at the anode. The current yield is considerably lowered if the temperature rises above 25° C.

If about 0.1 per cent. calcium chloride is mixed with the sodium chloride solution the yield increases noticeably; still more effective is the addition of 0.5 per cent. neutral

alkali chromate, whilst at the same time much more concentrated solutions of hypochlorite can be prepared. The progress of the electrolysis can be followed either by titration or by gas analysis; in the first case samples are taken every half-hour, and the hypochlorite contents determined iodometrically. As a by-product, the electrolyte contains chlorate; but this only occurs in very small quantity if the bath is cool and the amount of hypochlorite only a few per cent., and it can therefore be neglected. For the gas analysis observations, the electrolysis vessel is closed with a rubber stopper, and at regular intervals the escaping gases are collected; these consist of hydrogen and oxygen with traces of chlorine and hypochlorous acid which need not be determined. In order to be safe from explosions, a copper pipette (Hempel, *Gas Analysis*, Transl. of 3rd German edition, p. 159) is employed in place of the phosphorus pipette.

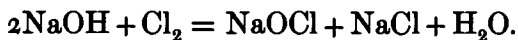
Since from observations of the current strength and time, the quantity of electricity is known, or still better the electrolytic gas may be directly determined by including a water voltameter, the corresponding quantities of hydrogen and oxygen are known. The difference between the hydrogen calculated and that collected from the bath is the amount used up in undesirable reduction; the amount of oxygen evolved gives the amount of the current action at the anode, which, instead of producing hypochlorite, has been employed in evolving useless oxygen. Very good examples of such gas analysis methods are found in the work of Oettel, 'Studies on the Electrolytic Formation of Hypochlorites and Chlorates' (*Z. Elch.* 1, 354-358).

The reactions in the bath can be explained fairly easily. The chlorine ions discharged at the anode are transformed into free chlorine, which dissolves in the liquid; at the cathode the sodium ions, discharged in equivalent quantity, react with the water.

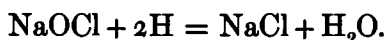


Hydrogen escapes and the dissolved caustic soda reacts

with the dissolved chlorine to produce sodium hypochlorite.

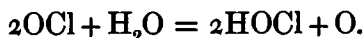


As soon as hypochlorite is present in considerable amount, it reaches the cathode and there becomes reduced.



Since only nascent hydrogen—just discharged H ions—and not free molecular hydrogen, acts upon sodium hypochlorite, a low cathode current density favours this undesirable reduction. With the same number of hydrogen ions discharged in unit time, the probability that they come instantaneously in contact with hypochlorite is greater when they are spread over a large surface, than when, crowded together, they make their appearance on a small surface; in the latter case it much more frequently happens that they unite with one another to give H_2 molecules. On this account, a high current density at the cathode is necessary. The cause of the decrease of the yield with increasing content of hypochlorite is to be found chiefly in the conditions just described, since here indeed the reduction increases.

At the anode, with low current densities, scarcely any gas is evolved at first; later, oxygen is given off in increasing amount; with high current density this behaviour is only apparent to a small extent. The explanation of this lies in the fact that the hypochlorite takes part in the electrolysis proportionally to its increase in the solution; for the process taking place at the cathode, this action is of no consequence, but at the anode are discharged, together with Cl ions, a constantly increasing number of OCl ions, which, as most of the acid radicles, combine with water with regeneration of the acid and evolution of oxygen.



Since now the OCl ions are discharged somewhat more easily than the Cl ions—the latter, however, are present in

much greater quantity—it is only necessary to impede the attempted discharge by a high current density, in order to diminish the wasteful oxygen evolution to a very small amount. For a good yield of hypochlorite, a high current density must prevail at the anode as at the cathode.

The difficulty for the preparation of highly concentrated hypochlorite solutions lies chiefly in the cathodic reduction. Certain artifices, which without involving the use of an actual diaphragm achieve its purpose, effect a very considerable improvement. It is clear that the reduction will almost cease if the cathode is covered with a thin layer of undisturbed electrolyte; for in this case fresh hypochlorite cannot continuously come within the sphere of the just discharged H ions, which are then evolved as hydrogen gas. To a certain extent such an undisturbed liquid layer at the cathode can be obtained by a thin porous coating lying upon it; for instance, if the salt solution to be electrolysed is contaminated with a very small quantity of calcium chloride, some calcium hydrate is deposited on the cathode; although this covering is broken away in flakes here and there by the hydrogen bubbles, still it always reproduces itself.

The object is attained much more perfectly than with calcium chloride, by addition of neutral alkali chromate. Owing to the reducing action at the cathode a thin coating of chromic hydrate (in alkaline solution), or chromic acid-chromic oxide (in weak acid solution), is produced, which is very efficient in preventing the reduction of the hypochlorite. The electrolysis with the addition of chromate is indeed one of the most ideal diaphragm processes which it is possible to imagine (E. Müller, *Z. Elch.* 7, 398–405). The observance of a low temperature in the electrolytic preparation of hypochlorites is necessary, on account of the fact that with increasing temperature, the transformation of hypochlorite into chlorate experiences a considerable acceleration; in the second place, the in-

crease of the destructive cathodic reduction at higher temperatures must also be considered.

Hypochlorites may also be prepared in a similar manner from potassium and barium chlorides; with calcium and magnesium chlorides the conditions are rather different, the difference being due essentially to the comparative insolubility of the hydroxides.

The preparation of sodium hypochlorite solution has considerable technical importance, since this solution can most advantageously replace bleaching powder for bleaching plant fibres. Moderate concentrations suffice for bleaching; generally a concentration of 1 to 5 grams, seldom of 10 to 12 grams 'available chlorine' per litre, is employed. Of great value is the fact that electrolytic bleaching liquids act much more quickly and powerfully than solutions of the same hypochlorite content prepared by purely chemical methods. This remarkable behaviour is evidently accounted for by the fact that in the electrolytic bleaching solutions, which contain no excess of alkali, a large proportion of the hypochlorite is present, not as salt, but as free acid. The artifice of diminishing the cathodic reduction by addition of calcium chloride or alkali chromate cannot be employed for technical bleaching solutions. The first means is not very effective, and the deposition of suitable calcium hydrate layers too dependent upon chance to make it advisable to put up with the considerable increase of resistance, and thus increased potential, of the bath-cell.

The second means, which is otherwise so perfect, cannot be employed on account of the strong yellow colour of the chromates.

Chlorates, Bromates, and Iodates.

References: F. Oettel, *Z. Elch.* 1, 474-480*; 5, 1-5; F. Foerster, *Z. Elch.* 6, 253-256, *J. pr.* 50, 244; 63, 141-166; F. Foerster, E. Müller, and Jorre, *Z. Elch.* 6, 11-22*; E. Müller, *Z. Elch.* 5, 469-473*; 7, 515; F. Foerster and H. Bischoff, *Z. Elch.* 4, 464-470; F. Foerster and H. Sonneborn, *Z. Elch.* 6, 597-604; F. Foerster and Jorre, *Z. anorg. Ch.* 23, 158-219; Haeussermann and Naschold, *Ch. Ztg.* 18, 857 (1894); W. Vaubel, *Ch. Ztg.* 22, 331

(1898); F. Haber and Grünberg, *Z. anorg. Ch.* **16**, 198, 329, 438; H. Wohlwill, *Z. Elch.* **5**, 61-76; **6**, 227-230; F. Foerster and E. Müller, *Z. Elch.* **9**, 171-185, 191-208*; F. Foerster and Gyr, *Z. Elch.* **9**, 215-226*; Pauli, *Z. Elch.* **8**, 474-478; J. Sarghel, *Z. Elch.* **6**, 149-158; R. Lorenz and A. Wehrlin, *Z. Elch.* **6**, 387-392, 408-410, 419-428, 437-441, 445-452; N. Lewin, *Z. Elch.* **6**, 464-466; F. Winteler, *Z. Elch.* **7**, 361; Elektrizitäts-Aktiengesellschaft, vorm. Schukert & Co. *D. R. P.*, Nos. 83,536 and 89,844; Kellner, *D. R. P.* No. 90,060; P. Imhoff, *D. R. P.* No. 110,420; Threlfall, *Brit. Patent*, No. 2,987 (1902); Corbin, *Brit. Patent*, No. 17,320 (1901).

3. POTASSIUM CHLORATE FROM POTASSIUM CHLORIDE.

Electrolyte: 100 gms. KCl, 1 gm. K_2CO_3 , 1 gm. $K_2Cr_2O_7$, dissolved in 250 gms. warm water.

Anode: Wire-gauze or sheet of platinum.

Cathode: Platinum foil, or nickel or copper sheet, though somewhat less favourable.

D_A : 20 amperes per 100 sq. cms.	} Distance apart of electrodes about 1 cm.
D_C : Unimportant, but at any rate greater than D_A .	

The bath is kept at a temperature between 40°C. and 60°C., and by a slow current of carbon dioxide the stirring of the liquid is effected, and a slightly acid reaction is ensured. At least 60 ampere hours must be passed through, since 1 ampere hour only yields 0.75 gram $KClO_3$. If a separation of $KClO_3$ has commenced during the electrolysis, then, after cooling the liquid, a considerable amount of potassium chlorate crystallizes out, which is purified by a single recrystallization. By evaporation of the mother-liquor to half its volume and then cooling, a second, less pure, batch of crystals is obtained. The current efficiency amounts to about 70 per cent. of the theoretical, and only begins to decrease considerably if more than half the KCl has been transformed into $KClO_3$. If the current efficiency be calculated from the amount of chlorate obtained in the solid form, the value deduced, although allowable on practical grounds, is incorrect, being too low on account of the portion remaining in the mother-liquor. The chlorate remaining in solution (together with hypochlorite which on account of the evaporation is present only in

traces) is determined by boiling a sample with ferrous sulphate and sulphuric acid, by which means it is reduced, and the excess of ferrous sulphate is determined by titration with permanganate, with addition of manganese sulphate.

Data for the efficiency of the separation of KClO_3 and KCl by crystallization are given in the following table:—

SOLUBILITY OF KClO_3 IN KCl SOLUTION AT 20°C .

Grams KCl per litre.	Grams KClO_3 per litre.	Specific gravity.
0	71.1	1.050
10	58	1.050
50	36.5	1.058
100	27	1.086
150	21.5	1.113
200	20	1.140
250	20	1.168

4. SODIUM CHLORATE FROM SODIUM CHLORIDE.

Electrolyte: 80 gms. common salt, 2 gms. soda crystals, 1 gm. sodium bichromate dissolved in 250 gms. water.

Other experimental conditions as in No. 3. Current efficiency over 70 per cent. The electrolyte is evaporated to a small volume, and the sodium chloride which separates

SOLUBILITY OF NaClO_3 IN NaCl SOLUTION AT 20°C .

Grams NaCl per litre.	Grams NaClO_3 per litre.	Specific gravity.
10	661	1.424
50	599	1.414
100	522	1.398
150	442	1.379
200	338	1.345
250	197	1.289
300	55	1.217

out is removed; on cooling the clear decanted solution, sodium chlorate crystallizes out, still contaminated with NaCl and Na_2CrO_4 ; a complete purification of small quantities is impracticable on account of the great solubility of sodium chlorate. Yield of material about 70 per cent.

5. POTASSIUM BROMATE FROM POTASSIUM BROMIDE.

Electrolyte: 25 gms. KBr, 0.2 gm. K_2CrO_4 dissolved in 100 c.c. water.

Anode: Platinum sheet or gauze.

Cathode: Platinum or nickel sheet.

$D_A = D_C = 10\text{--}12$ amps. per 100 sq. cms.

The bath is kept at 35° to 45° C., and at least 25 ampere hours are employed; then the solution is evaporated to about 40 c.c. and allowed to crystallize by cooling.

Current efficiency over 90 per cent., yield of material over 70 per cent. of theory.

100 parts water dissolve at	0°C.	3.1	} parts KBrO_3 .
	20 "	7.0	
	60 "	22.8	
	100 "	49.8	

6. SODIUM BROMATE FROM SODIUM BROMIDE.

Electrolyte: 40 gms. NaBr, 0.2 gm. Na_2CrO_4 , 100 c.c. H_2O .

Other conditions as in preparation of potassium bromate.

The current efficiency exceeds 90 per cent. After passage of at least 50 ampere hours the electrolyte is evaporated to 40 c.c. and allowed to crystallize out. The same difficulties of purification are experienced as with sodium chlorate.

Yield of material 60 to 70 per cent.

100 parts water dissolve at	0°C.	27.5	} parts NaBrO_3 .
	20 "	34.5	
	60 "	62.5	
	100 "	90.9	

7. POTASSIUM IODATE FROM POTASSIUM IODIDE.

Electrolyte: 25 gms. KI, 1 gm. KOH, 0.2 gm. K_2CrO_4 , 100 c.c. H_2O .

The other conditions as in the preparation of potassium bromate.

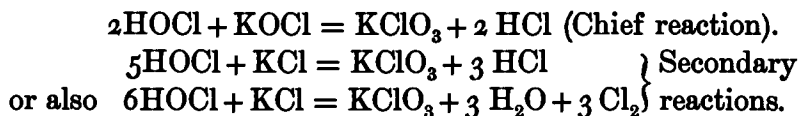
Current efficiency over 90 per cent., yield of material over 80 per cent. of the theory.

100 parts water dissolve at	0° C.	4.7	} parts KIO_3 .
	20 "	8.1	
	60 "	18.5	
	100 "	32.2	

The preparation of sodium iodate from sodium iodide proceeds in the same manner and with about the same yield as potassium iodate.

100 parts water dissolve at	0° C.	2.5	} parts $NaIO_3$.
	20 "	9.1	
	60 "	20.9	
	100 "	33.9	

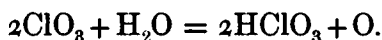
The processes taking place in the electro-chemical formation of chlorates from chlorides in neutral or very weak acid solution, have been satisfactorily explained so far as the chief facts are concerned, although some points of secondary interest remain unsolved. Hypochlorite always forms the first step of the oxidation (concerning this see Ex. No. 2). In the neighbourhood of the anode, where a weak acid reaction and thus free hypochlorous acid is always to be found, both hypochlorite and chloride are oxidized to chlorates by the free hypochlorous acid:



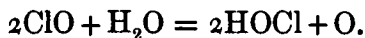
Thus hypochlorite, which is fairly stable in alkaline solution, is transformed by free hypochlorous acid into chlorate in neutral and still more in weak acid solutions

(presence of bicarbonates or carbonic acid); and this reaction proceeds slowly at ordinary temperatures, but very quickly at 50° to 60° C. On this behaviour rests one of the reasons why in the preparation of hypochlorite the bath is cooled, whereas for chlorates it is warmed; the other reason being, that chlorates are transformed at the anode at low temperatures into perchlorates, but not at higher temperatures.

Hypochlorites are strongly reduced at the cathode in nearly neutral solutions, but the chlorates only very slightly. Since, however, the chlorates are formed from the previously produced hypochlorites, it is necessary to limit this cathodic reduction as much as possible, as by the addition of alkali chromate to the electrolyte. On the other hand, hypochlorite is quickly transformed into chlorate at higher temperatures, so that only a small hypochlorite concentration is necessary, and consequently with high current density the cathodic reduction can be kept within moderate limits, and even without a special artifice, satisfactory yields of chlorate obtained. In proportion as the solution becomes weaker in chloride and more concentrated in chlorate, the chlorate takes part in the electrolysis and gives rise to an evolution of oxygen at the anode:



However, this decomposition only occurs to a small extent; as noted before, the hypochlorite behaves similarly:



As can be proved the evolution of oxygen at the anode in the preparation of chlorates is due chiefly to the hypochlorite, and since this, as intermediate product, must always be present up to a certain concentration, a moderate loss of current by oxygen evolution at the anode cannot be avoided. A direct oxidation of chlorine or hypochlorous acid to chloric acid, if it occurs at all, only does so to a very small extent. For the preparation of chlorates the conditions can therefore be summarized as follows:—

(1) Diminution of the cathodic reduction by very high current density at the cathode, or still more efficiently, by addition of alkali chromate.

(2) The solution should be made weakly acid for the production of larger quantities of hypochlorous acid. Current of CO_2 .

(3) A sufficiently large volume of the solution in proportion to the current and an efficient mixing of the electrolyte should be ensured, in order that the secondary reactions which demand a certain time may be completed.

(4) Temperature of at least 40°C . must be attained, firstly, to assist the secondary reactions, secondly, to prevent formation of perchlorate, and finally to diminish the potential of the bath.

In order to demonstrate the correlated processes, the accompanying curves (Fig. 6) due to F. Foerster will be of assistance. Electrolyte: 500 c.c. of a NaCl solution containing 30 gms. per 100 c.c., which was electrolysed with 4.5 amperes, at a current density of $D_A = 7.5$, $D_C = 1.8$ amperes per 100 sq. cms.

As abscissae the time is given in hours, as ordinates the amount of active oxygen in decigrams corresponding to the amounts of hypochlorite and chlorate experimentally determined, and also the proportion of the current, expressed in percentage, used for cathodic reduction and oxygen evolution at the anode.

The above conditions hold substantially not only for the preparation of chlorates but also for bromates and iodates, the chief difference being that here satisfactory results cannot be attained without addition of alkali chromate. For not only are the hypobromites and still more the hypoiodites very easily reduced, but even the bromates and iodates undergo considerable reduction, which is not the case with the chlorates. The transformation of hypobromites and hypoiodites into bromates and iodates occurs quickly even at ordinary temperatures; one need not fear the formation of periodates, and but little that of

perbromates; the electrolysis can therefore be carried out without external warming, and the temperature of the bath

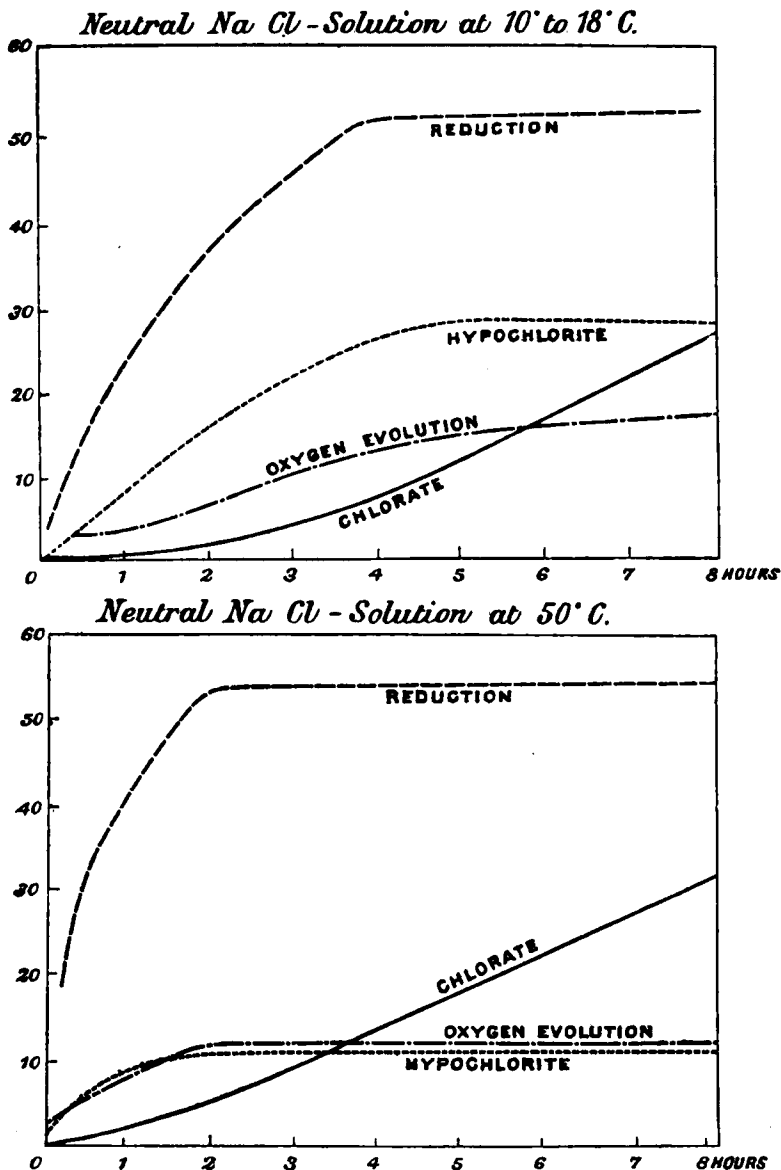


FIG. 6.

should not be allowed to rise above 50° C., since otherwise the destructive reducing action becomes predominant.

Technically, during the last few years, the electro-chemical preparation of chlorates has become so generally adopted as now to have almost completely displaced the previous manufacture by purely chemical means. The electro-chemical method, however, requires a large expenditure of energy—for preparation of 1 kilo. KClO_3 , 12 to 18 h.p. hours are necessary; it is therefore confined to those places where large water-power is available. Commercial electrolytic potassium chlorate contains no trace of perchlorate and is almost chemically pure; sodium chlorate, on the other hand, usually contains, for reasons which can be easily seen, a considerable amount of common salt as impurity.

Perchlorates.

8. POTASSIUM PERCHLORATE FROM POTASSIUM CHLORATE.

References: F. Foerster, *Z. Elch.* 4, 386-388*; F. Winteler, *Z. Elch.* 5, 50-51, 217-221*; E. Müller, *Z. Elch.* 7, 509-516.

Electrolyte: Solution of KClO_3 saturated at temperature of room (about 60 grams KClO_3 per litre). Should the solution be somewhat alkaline, or become so during the electrolysis, it should be acidified weakly by addition of a few drops of dilute sulphuric acid.

Anode: Wire-gauze or foil of platinum.

Cathode: Platinum foil or, less suitable, copper sheet.

D_A : 8 to 12 amps. per 100 sq. cms.

$D_C = D_A$ or higher.

The temperature of the bath should not exceed 25°C . as a maximum; thus a considerable cooling with water or ice is necessary. Continuous stirring is harmful; mixing from time to time is, however, advantageous. It is convenient to keep the electrolyte approximately saturated with KClO_3 by the following arrangement: In a small funnel with a long obliquely-cut neck, a little glass wool is lightly pressed, and above this potassium chlorate crystals are placed; the whole is so immersed in the bath, a narrow

beaker, that the funnel comes completely or partly under the surface of the liquid. At the anode a small evolution of oxygen is noticeable from the commencement; the escaping gas is strongly ozonized. When the experiment has been in progress some little time and the electrolyte is saturated with KClO_4 , fine crystals of perchlorate fall from the anode to the bottom of the vessel. The current efficiency is about 80 per cent.

In 100 parts water at	0° C.	0.7	} parts KClO_4 dissolve.
	50 "	6.4	
	100 "	19.9	

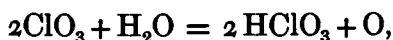
Potassium perchlorate can be obtained indirectly, using sodium perchlorate as an intermediate product, with smaller potential difference and still better yield. Under the same conditions as above a solution of 20 to 50 grams sodium chlorate in 100 grams water is electrolysed. Technical sodium chlorate containing sodium chloride is quite suitable for the experiment if, in case it should become alkaline by loss of chlorine at the anode, the solution is made weakly acid with a few drops of sulphuric acid. The current yield of NaClO_4 exceeds 90 per cent. until the content of NaClO_3 in the electrolyte has decreased to 10 per cent. On account of its great solubility, sodium perchlorate can only be separated with difficulty; it is therefore transformed into the very insoluble potassium salt by addition of a cold saturated solution of KCl , in amount corresponding to that calculated from the number of ampere hours employed for the electrolysis; after some time the precipitated KClO_4 is filtered off; it is, however, when thus prepared, always contaminated with a little KClO_3 . Barium perchlorate can be prepared by the same methods as the alkali perchlorates. A cold saturated solution of commercial barium chlorate (approx. 320 grams $\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{O}$ per litre) is employed; a small contamination with BaCl_2 is of no consequence. The current efficiency at first exceeds 70 per cent., but sinks finally to 20 per cent., when 90 per cent. of the chlorate has been transformed into perchlorate. The

ratio of the solubilities of barium chlorate and perchlorate in water does not admit of a simple separation. By means of alcohol, however, nearly pure barium perchlorate can be easily prepared with a yield of material of over 80 per cent.; the electrolyte is evaporated to dryness and the residue extracted with boiling 99 per cent. alcohol, which easily dissolves the perchlorate, but scarcely at all the chlorate and chloride; by distilling off the alcohol barium perchlorate remains behind.

The electrolytic oxidation of chlorates to perchlorates depends upon the reaction,



whereby 2 discharged chloric acid ions unite with water to give 1 molecule perchloric acid and 1 molecule chloric acid, which form salts with the alkali coming from the cathode. This reaction is confined to low temperatures; the warmer the solution, the more easily occurs the characteristic transformation of the acid radicles



and wasteful evolution of oxygen replaces the oxidation of the chlorate. The reducing action at the cathode scarcely comes into consideration, since at ordinary temperatures and with high current density neither chlorates nor perchlorates in neutral solution suffer a measurable cathodic reduction. Bromates cannot be electrolytically transformed into perbromates, whilst the preparation of periodates from iodates only goes incompletely.

Perchlorates are commercially prepared by electrochemical means.

9. PREPARATION OF AMMONIUM PERSULPHATE FROM AMMONIUM SULPHATE.

References: H. Marshall, *Chem. Soc.* 59, 771-786 (1891); Berthelot, *Compt. rend.* 114, 876 (1892); K. Elbs, *J. pr.* 48, 185-188* (1893), *Z. Elch.* 2, 162-163; K. Elbs and O. Schönherr, *Z. Elch.* 1, 417-420; 2, 245-252; A. R. Foster and E. F. Smith, *Amer. Chem. Soc.* 21, 934 (1899).

Bath: A porous pot of 80 to 150 c.c. capacity stands in

a beaker; a lead cooling spiral as cathode surrounds the porous pot.

Anode: Platinum wire spiral of 1 to 2 sq. cms. surface.

Cathode: Lead tube with soldered copper wire for current connexion.

D_A : 500 to 1,000 amps. per 100 sq. cms.

D_C : As low as possible, to save voltage and excessive evolution of heat.

Anode liquid: Cold saturated ammonium sulphate solution.

Cathode liquid: Mixture of 1 volume concentrated sulphuric acid and 1 to 2 volumes water.

Good cooling should be assured, the temperature of the anode chamber remaining always between 10° and 20° C.; this is effected by supplying the spiral tube with cold, or better, iced water. The anode liquid is kept approximately saturated with ammonium sulphate, by suspending in the anode portion of the cell a small test-tube pierced with a number of small holes and filled with the salt. A current of highly ozonized oxygen gas is slowly evolved at the anode; the electrode dips about halfway down in the liquid contained in the porous pot. From time to time, after intervals of three or four hours, the electrolysis is stopped, and the contents of the porous pot filtered through glass wool; the crystals thus separated are dried on a porous plate, whilst the filtrate is shaken with crystallized ammonium sulphate and thus again saturated, after which it is poured back into the porous pot. The liquid in the cathode portion of the cell becomes neutralized as a result of the migration of sulphuric acid anions away from it and that of ammonium ions into it, and before it becomes alkaline must be syphoned off and replaced by fresh sulphuric acid. On the other hand, the anode liquid becomes poorer in ammonia and more concentrated in sulphuric acid, on account of the migration of the ammonium ion out of it and that of the sulphuric acid anion into it; this alteration is not compensated for by the separation of ammonium persulphate and the occasional saturation of

the solution with ammonium sulphate; it is consequently necessary about every two operations to add to the anode liquid by means of a funnel with a capillary tube, with cooling, a quantity of ammonia, saturated with ammonium sulphate, sufficient to nearly neutralize the free acid. The precipitate which is thus formed consists of ammonium persulphate, and is poured with the liquid into the porous pot. At the first operation the separation in the porous pot is rather small, at the later ones considerable, since it is necessary for the liquid to become saturated with ammonium persulphate before a separation of the solid salt can commence; in the later operations this is the case at the start. When the experiment is finished, the anode liquid is either preserved for later experiments, or the persulphate contained in it is recovered in the form of a crystalline precipitate of potassium persulphate by careful addition of a moderately concentrated solution of potassium carbonate. It is very important before each experiment to wash the anode with water and heat it to glowing. The current efficiency exceeds 70 per cent., the yield of material 60 per cent. The raw product contains as chief impurity about 5 per cent. of ammonium sulphate; the salt can be obtained crystallized in a pure and fine condition, although necessarily with considerable loss, if water of 50° C. is quickly saturated with the salt and then allowed to cool slowly to a low temperature. Ammonium persulphate can only be preserved from decomposition in a completely dry condition. For the quantitative determination, the solution of persulphate is poured into an excess of strongly acid ferrous ammonium sulphate, and the excess of ferrous salt titrated back with permanganate. It must be observed, however, that, in the cold, Mohr's salt is not momentarily oxidized by the persulphates, but that the reaction takes several minutes¹. In the preparation of persulphates, hydrogen peroxide and its derivatives are also formed in the anode chamber; these can be determined directly by means of

¹ Cf. Le Blanc, *Chem. News*, 81, 38 (1900).—Tr.

permanganate. In order, therefore, to follow the course of the electrolysis, samples of the anode liquid are titrated first with permanganate, then reduced with ferrous ammonium sulphate and titrated back with permanganate; in this way the first determination gives the content of hydrogen peroxide, the second that of persulphate. With the apparatus described above and under the same conditions, potassium persulphate can also be prepared. In consequence of the difficult solubility of potassium sulphate the method is not very satisfactory; however, on account of the still smaller solubility of potassium persulphate it is simple and effective. In small quantity, potassium persulphate can be easily prepared in the apparatus shown in Fig. 7.

A wide boiling-tube (P) contains the electrolyte, a saturated solution of potassium sulphate in sulphuric acid of

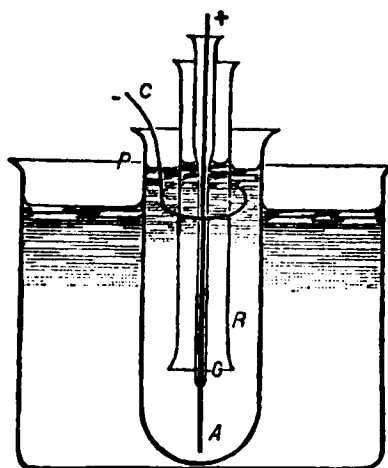


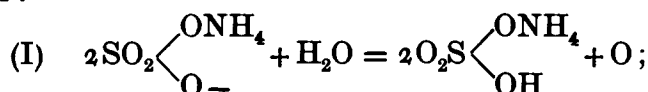
FIG. 7.

1.2 to 1.3 sp. gr.; the anode (A), a platinum wire (to be ignited before each experiment), surrounded for the greater part of its length by a drawn-out glass tube (G), passes nearly to the bottom of the tube, whereas the cathode (C), a looped platinum wire, is situated above, near the surface of the liquid. In order to prevent the oxygen-gas bubbles evolved at the anode from carrying the liquid away from the

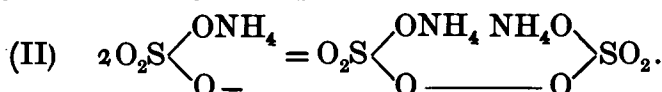
neighbourhood of the anode to the cathode, they are collected by the widened-out glass tube (R), and thus led away. For cooling purposes the whole apparatus is immersed in a beaker of cold water. The most suitable current density at the anode is 100 amperes per 100 sq. cms. with a current of 1 to 2 amperes; a thick deposit of potas-

sium persulphate will already have collected in the under part of the vessel after ten minutes have elapsed.

The formation of persulphates at the anode is explained by the fact that in concentrated solutions of sulphates, for instance of ammonium sulphate, not only the anions SO_4 but also the anions HO_4SO_4 are present, and the greater the concentration and current density, the greater the extent to which they are discharged. The discharged anions react in two ways: either they combine with the water:

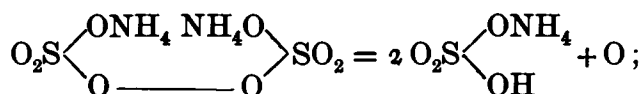


or by addition they form persulphate:



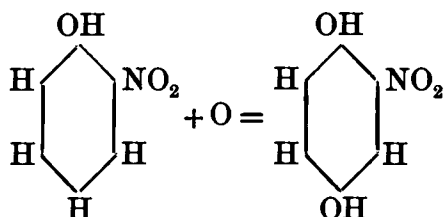
High current density at the anode favours the reaction (II), and consequently for the preparation of persulphates very high current densities are employed.

The properties of the persulphates agree well with the above representation of their structure; they are derivatives of hydrogen peroxide. Upon warming, in aqueous solution, both the acid and its salts evolve oxygen:

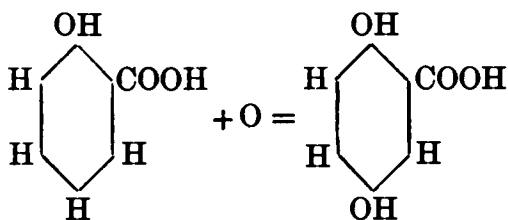


their preparation demands therefore a low temperature.

The persulphates are slow-acting, but strong-oxidizing agents, cause the separation of the free halogens from their hydracids, oxidize alcohol to aldehyde, *o*-nitrophenol to nitro-hydroquinone:



and salicylic acid to hydroquinone carboxylic acid :



Since persulphates are particularly suitable for many oxidations, they are commercially prepared at several places.

B. EXPERIMENTS WITH SOLUBLE ANODES.

10. CUPROUS AND CUPRIC OXIDES FROM COPPER.

Reference: R. Lorenz, Z. anorg. Ch. 12, 436.*

The cells (I and II) are connected in series in the same circuit; both contain anodes of sheet-copper and cathodes of tinned iron or ordinary sheet-iron, placed about 4 cms. from each other and from the bottom of the beaker. In cell I the electrolyte is a half-saturated solution of common salt, in II a half-saturated sodium sulphate solution.

$D_A = D_C = 2$ to 4 amperes.

Yellow cuprous hydrate separates between the electrodes in cell I, whilst in II bluish-green cupric hydrate is formed, in both cases with almost quantitative yield. If the experiment is altered so that the cells are kept throughout nearly at the boiling-point, then in I red cuprous oxide separates, whilst in II black cupric oxide is produced, again in almost quantitative amounts; the cuprous oxide is contaminated with some metallic copper¹.

The following explanations of the above experiments are given. The discharged anions in I form cuprous chloride,

¹ For the arrangement of the experiment in the form described, the author is indebted to instructions received several years ago in a letter from Dr. F. Oettel.

in II copper sulphate; the cuprous chloride dissolves in the salt solution, the cupric sulphate in the sodium sulphate solution; both meet with the sodium hydrate which is formed in equivalent amount at the cathode, and thus sodium chloride and sodium sulphate are regenerated, whilst in I cuprous hydrate, in II cupric hydrate is precipitated. Upon heating, these hydrates become anhydrous and cuprous and cupric oxides are obtained.

In analogous manner, hydrated zinc oxide, cadmium oxide, and ferrous oxide can be prepared in sodium chloride, or sulphate solutions, from the corresponding metals.

In order not to contaminate the precipitates with particles falling from the anode or cathode, the electrodes can be enclosed in a muslin bag. This method can in many cases be of much practical use.

11. WHITE LEAD FROM METALLIC LEAD.

References: W. Borchers, *Z. Elch.* 3, 482-485; Luckow, *Brit. Patent*, No. 14,801 (1895); Le Blanc and Bindschedler, *Z. Elch.* 8, 255-264* (1902); Isenburg, *Z. Elch.* 9, 275-283* (1903).

Electrolyte: 12 grams sodium chlorate and 3 grams sodium carbonate dissolved in 1 litre of water.

Anode and cathode: Lead plates, 10 cms. from each other and from the bottom of the cell.

$D_A = D_C = 0.5$ amperes per 100 sq. cms.

The electrolysis is carried out at the temperature of the room, a slow current of CO_2 being passed through the solution from a drawn-out tube behind the cathode, so that the electrolyte is not stirred up. The white lead flows down in thick clouds from the anode to the bottom of the cell. The yield is very good. The electrolyte contains two salts in very dilute solution; the one which is present in four-fifths the total amount has an anion which forms a soluble salt with the anode metal, lead chlorate, and thus causes the anode to pass into solution; the other, present only to the extent of one-fifth the total amount, whose anion forms an insoluble salt, lead carbonate, and thus

causes the precipitation. As a result of employing these proportions the insoluble salt does not deposit directly on the anode, but is precipitated at some distance from it, and thus does not form an insoluble crust on the electrode, but falls as a finely divided homogeneous powder in the electrolyte. The caustic soda produced at the cathode continuously regenerates the carbonate, by the current of carbonic acid gas passing through the solution. In a similar manner, lead chromate, basic copper carbonate, copper phosphate and other insoluble salts can be obtained from the heavy metals. The electro-chemical preparation of white lead according to the Luckow method has attained commercial importance.

12. LEAD DISULPHATE (PLUMBIC SULPHATE) FROM METALLIC LEAD.

References: K. Elbs, *Z. Elch.* 6, 47; K. Elbs and F. Fischer, *Z. Elch.* 7, 343-346*.

A large glass vessel serving as anode chamber, and a porous cell suspended in it for the cathode chamber, are filled with sulphuric acid of 1.7-1.8 sp. gr.

The anode consists of two bright lead plates, the cathode of a lead tube coiled, with long ends projecting over the sides of the glass vessel; these are connected with rubber tubing for the inlet and outlet of the water cooling. (The rubber tube must not be exposed to the ozonized gases evolved at the anode, since it becomes destroyed in this way.) The electrolysis is carried out with a current density of 2 to 6 amperes per sq. decimeter, and the temperature in the anode portion is prevented from rising above 30° C. by occasional cooling in the cathode portion of the cell. (The formation of lead peroxide by hydrolytic dissociation of the disulphate occurs the more readily the higher the temperature; at the same time the useless evolution of oxygen increases, so that practically the highest permissible temperature is about 40° C.)

Generally, the anode liquid soon becomes turbid and a white precipitate settles down slowly on the bottom of the anode chamber; this is impure plumbic sulphate, whilst the pale yellowish-green coloured liquid is a solution of lead disulphate in sulphuric acid. Should brown spots of lead peroxide form on the anode plates during the electrolysis, the anode should be withdrawn from the solution, washed with acidified sodium nitrite solution, rubbed dry with sand, and replaced. It is advantageous to employ a large quantity of anode solution, since it becomes concentrated during the experiment, and the conductivity decreases the more quickly, the smaller the amount of the liquid. However, with a little care, it is possible to dilute the anode solution during the electrolysis if its resistance has become too high; this is effected by allowing dilute sulphuric acid to flow slowly down the side of the vessel containing the solution, which has previously been well cooled. After some hours the porous pot and electrodes are removed from the apparatus, any salt adhering to the anode having been rubbed off; the deposit at the bottom is now stirred up and the whole contents of the anode chamber poured into a well-stoppered bottle. Here the greater part of the plumbic sulphate is deposited at the bottom in a few days as a slime; on the walls of the vessel and on the surface of the slime a considerable amount of the salt often separates in the form of white indefinitely crystallized grains. The current yield varies and amounts in the mean to 60 per cent. of the theory, when determined as impure plumbic sulphate. In order to obtain the dry lead disulphate, the sulphuric acid is poured off and the deposit placed upon porous plates, which are kept over sulphuric acid in a desiccator for some hours; the mass is then transferred to fresh porous plates, and again allowed to remain for some time in the desiccator, the process being continued until a quite dry powder is obtained, which does not alter when kept in dry air. The substance thus obtained contains from 60 to 85 per cent. of plumbic

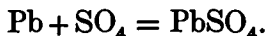
sulphate, the remainder being plumbous sulphate. The granular substance which separates is much purer; fairly considerable amounts of it can be obtained, if, before stopping the electrolysis, the temperature be raised for about an hour to 40 or 50 degrees and the approximately clear anode liquid be then syphoned off and allowed to stand to cool in a well-stoppered vessel. The salt, which is more easily soluble at a higher temperature, then separates slowly in granular crusts, which contain between 85 and 99 per cent. of lead disulphate. The deposit at the bottom of the anode chamber is worked up in the usual way. No satisfactory method of purifying the whole amount of the reaction product has yet been discovered. If the formation of lead disulphate is progressing well, the lead anodes go steadily into the solution and become in this way bright, just as though they were freshly amalgamated, and they appear in colour and polish more like zinc than lead. Lead disulphate is a quite indefinite crystalline powder, white, but generally slightly yellowish, difficultly soluble in concentrated sulphuric acid and pyro-sulphuric acid giving a pale yellowish-green coloured solution. With all solvents otherwise generally employed it either undergoes combination or is insoluble. Water immediately decomposes lead disulphate into sulphuric acid and lead peroxide or its hydrate. Dilute sulphuric acid produces a hydrolytic decomposition which is the more rapid the greater the dilution of the acid; the limit for this reaction lies at about 1.650 to 1.653 sp. gr. at ordinary temperatures. The more concentrated the sulphuric acid, the higher the temperature which the solution is able to stand; for instance, with acid of 1.70 sp. gr., it can be heated to about 50° C. before lead peroxide separates. In acid of 1.80 and above the hydrolytic decomposition does not occur; here at about 100° C. evolution of oxygen takes place.



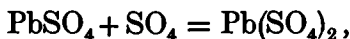
Plumbic sulphate is a strong oxidizing agent which in

most cases acts in the same manner but more powerfully than lead peroxide.

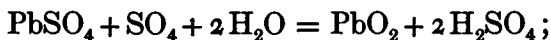
The formation of plumbic sulphate on a lead anode in concentrated sulphuric acid, whereas in dilute acid, a film of lead peroxide is produced which makes the lead anode unattackable, can be easily understood. At first, under all conditions, plumbous sulphate is formed:



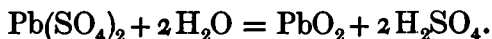
From this, either plumbic sulphate can be formed according to the equation



or lead peroxide can be directly produced,



in any case lead peroxide is the only product in presence of dilute acid, since under these circumstances plumbic sulphate is hydrolytically decomposed



As soon, however, as the sulphuric acid is sufficiently concentrated to hinder such a hydrolytic decomposition, the otherwise unattackable lead anode becomes soluble; for instead of being covered with a surface layer of insoluble lead peroxide, the moderately soluble lead disulphate is produced, the anode takes a metallic polish and is dissolved with formation of the sulphate of tetravalent lead.

13. PRODUCTION OF PURE COPPER FROM BRASS.

Electrolyte: 1 gram copper sulphate, 1 gram zinc sulphate, 4 to 8 c.c. concentrated sulphuric acid, 300 c.c. water.

Anode: Sheet of brass or large spiral of brass wire.

Cathode: Lead plate rubbed up with sand and coated on one side with paraffin.

$D_A = 0.5$ to 1 ampere per sq. cm.

$D_C = 2$ to 4 amperes.

The electrolyte is kept in steady motion by a slow current of carbonic acid gas; the amount of current should not be less than 10 ampere hours. The copper deposit can be easily removed as a coherent sheet by bending the lead cathode; the purity of the deposited copper can be recognized with ease from the fineness of its colour.

Very different current densities should be employed, neutral solutions, different concentration, and different proportions of zinc and copper sulphates in order to find out the influence of these variations; the appearance of the copper deposit at once shows when the conditions for the separation of pure copper are no longer fulfilled.

Brass has a very varying composition and contains as an average 60 per cent. Cu and 40 per cent. Zn, and besides often some lead and even iron. The SO_4 ions discharged at the anode produce sulphates of Cu, Zn, Pb (and Fe). PbSO_4 separates at the anode as a precipitate—anode slime—and does not come into further consideration.

On the other hand, the cations Cu^{++} , Zn^{++} , and Fe^{++} go into solution; but besides these H^+ ions are abundantly present in the acidified solution. The Cu^{++} ions are by far the most easily discharged, the H ions with more difficulty, but most difficultly of all the Fe and Zn ions.

Up to a certain current density the copper ions alone are discharged; if the current density be raised or if the solution become poorer in copper, so that the Cu ions in the immediate neighbourhood of the cathode are no longer sufficient for carrying the current, then, besides the copper deposition, an evolution of hydrogen is noticeable—the copper deposit still remains pure. Only at still higher current densities when even these are insufficient for the purpose, do the zinc ions begin to be discharged—the copper deposit is contaminated by zinc, and becomes gray and spongy. The electrolysis offers, therefore, a most satisfactory means of separating pure copper from copper alloys directly in the metallic condition, a result unattainable by other methods. In the electrolytic refining of

copper, practical use is made of this behaviour, on a very large scale, as also in the quantitative determination of copper by electrolysis.

II. EXAMPLES FROM ORGANIC CHEMISTRY

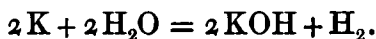
A. ELECTROLYSIS OF ORGANIC ACIDS.

References: H. Kolbe, *A.* 69, 257-294*, *Chem. Soc.* 2, 157-184 (1849); Brazier and Gosleth, *Chem. Soc.* 8, 222 (1851); Murray, *Chem. Soc.* 61, 10-36 (1892); M. J. Hamonet, *Compt. rend.* 123, 252*, W. Löb, *Z. Elch.* 3, 42; C. Schall, *Z. Elch.* 3, 83; 6, 102; C. Schall and R. Klien, *Z. Elch.* 5, 256-259; P. Rohland, *Z. Elch.* 4, 120-123; J. Petersen, *Z. ph. Ch.* 33, 90-120*, 295-325*, 698-720; K. Elbs, *J. pr.* 47, 104 (1893); K. Elbs and K. Kratz, *J. pr.* 55, 502* (1897); J. Troeger and E. Ewers, *J. pr.* 58, 121 (1898); 59, 464 (1899); A. Kekule, *A.* 131, 79 (1864); Aarland, *J. pr.* 6, 256 (1873); Crum Brown and J. Walker, *A.* 261, 107-128*, or *Trans. R. S. Ed.* 36, 211-224 (1891); *A.* 274, 41-71*, or *Trans. R. S. Ed.* 37, 361-379 (1893); G. Komppa, *C.* 70, ii, 1016 (1899); J. Walker and W. Cormack, *Chem. Soc.* 77, 375 (1900); W. V. Miller and H. Hofer, *B.* 27, 461 (1894); 28, 2427-2438* (1895); *Z. Elch.* 4, 56; H. Hofer, *B.* 33, 650-657 (1900).

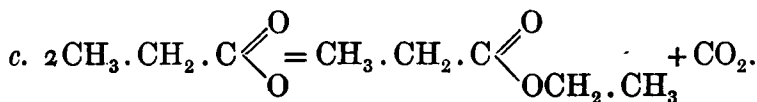
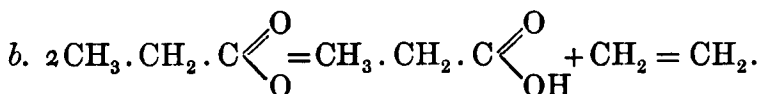
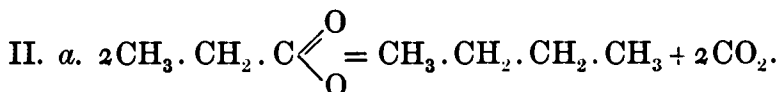
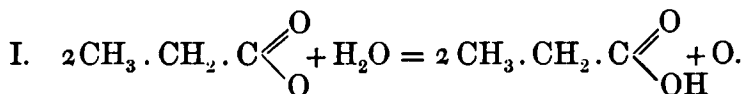
For the electrolysis of organic acids we have to deal only with their salts, especially the alkali salts; the free acids are generally but little dissociated and conduct therefore exceedingly badly. Extended experiments have been carried out on the electrolysis of the alkali salts of the simpler organic acids, and the processes can be considered from a general standpoint, but the causes of the reactions which occur in some special cases have been discovered only to a small extent. An example will show most clearly the essential reactions, unattackable electrodes being of course considered.

ELECTROLYSIS OF AN AQUEOUS SOLUTION OF POTASSIUM PROPIONATE $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOK}$.

Process occurring at the cathode :



Processes at the Anode :



We are here only interested in the reactions occurring at the anode; these fall into two groups:

I. Reaction of the discharged anion with the water; acid is regenerated just as is usual with most of the inorganic acids, and oxygen becomes available; this escapes partly as gas but causes also secondary reactions of oxidation, the nature and amount of which depend on the particular electrolyte, as also on the temperature, concentration and similar conditions.

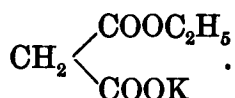
II. Interaction of the discharged acid anions in three different ways:

a. Two anions give up their carboxyl residues as two molecules carbonic acid; the hydrocarbon residues then link themselves into a saturated hydrocarbon; for instance, butane is formed from propionic acid.

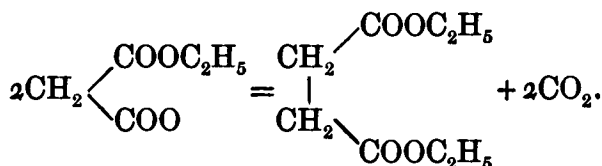
b. Two anions react in such a way that one molecule of CO_2 is spit off, the other takes a H atom from the hydrocarbon residue thus left and thus regenerates acid, and in this manner an unsaturated hydrocarbon is formed from the first anion. Thus from propionic acid we get ethylene.

c. Two anions undergo double decomposition with spitting off of carbonic acid from one which then as alkyl residue unites with the other, producing a molecule of an

ester. Thus we get the ester of the acid with the alcohol of the next lower series, from propionic acid the ethyl ester of propionic acid. The equations given under I and II include really all observations which have been made up to the present on the electrolysis of the alkali salts of the organic acids. Whatever other substances are obtained must be looked upon as the products of further reaction between the first typical reaction products. The application of the equations to more complicated cases is by no means difficult. Consider, for instance, the potassium salt of ethyl malonic acid ester,

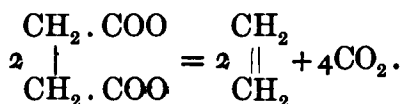


Esters are not electrolytes, and consequently the carboxyl group which has been esterified does not take part in the electrolysis, but only that which has formed a salt; if the reaction occur according to II α , then the diethyl ester of succinic acid must be formed:



This is indeed actually the case. The preparation of the diethyl ester of adipic acid from the potassium salt of the acid ethyl ester of succinic acid, is a good representation of this process according to the equation II α (No. 17), as is also the preparation of ethane from sodium acetate according to No. 14. The reaction II b is represented by the example No. 15 for the preparation of ethylene from propionic acid, II c by No. 16, preparation of the trichlor-methyl ester of trichloroacetic acid from trichloroacetic acid. It remains now to answer the question: under what conditions does the one or other of the reactions given under I and II occur? Here also a general rule can be given. If the salt solution is dilute, or if the current density is

low or if both occur, then the conditions for the fulfilment of case I are favourable, since the residues come in contact chiefly with water molecules and not with similar residues; on the other hand, if the solution is concentrated, and the current density high, then the discharged ions are confined to a small space, and the probability is great that they will meet with residues of the same nature and not with water and will interact as shown in II *a*, *b*, *c*. Moreover high temperature favours the reaction of the residues with water in the sense of equation I, low temperature on the other hand in the sense of II; this influence is so great that at 100° C. I is almost quantitatively fulfilled, whatever the other experimental conditions. Finally, the chemical nature of the acid comes particularly into consideration. Acids of the aromatic series react almost without exception entirely, or nearly entirely, according to I, acids of the fatty series according to the above-mentioned conditions chiefly according to I and II. If the change occur according to II, then it depends almost entirely on the nature of the acid and scarcely at all on the other conditions whether the reaction occur according to II *a*, *b*, or *c*—if a paraffin, an olefine, or an ester is obtained as chief product. Seeming exceptions can be easily explained from the chemical nature of the substances, an example of which is given in the behaviour of succinic and acetic acids. Sodium succinate reacts on electrolysis under suitable experimental conditions chiefly according to II *a*; the product is, however, not a paraffin, but an olefine, namely ethylene:

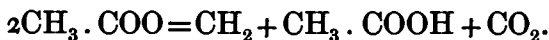


Without doubt the explanation of this lies in the fact that, after splitting off the CO₂ the residue $\text{CH}_2\text{---CH}_2$ is capable of existence as ethylene, and consequently the interaction of two hydrocarbon residues to form a saturated

hydrocarbon does not occur. The converse occurs with acetic acid, which yields as normal product ethane according to II *a*:

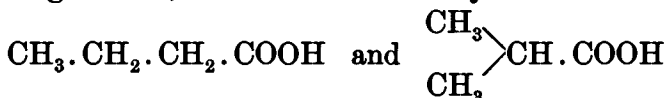


And in addition, but to quite a small extent ethylene. This secondary product must be ascribed to a portion of the discharged anions reacting according to II *b*:



Now methylene is not capable of existence, and from all known chemical reactions which should yield methylene, the next homologue ethylene $\text{CH}_2 = \text{CH}_2$ is obtained instead of this substance; this also holds for electrolysis.

No regularities have yet been found for the occurrence of one or other of the several reactions given in *a*, *b*, *c* under II. In this connexion the results can by no means be foretold. Homologous acids often behave quite differently, isomeric acids on the other hand often with perfect similarity. Thus acetic acid yields as chief product ethane according to II *a*, the next homologue, propionic acid, quite exceptionally does not yield *n*-butane, but ethylene, according to II *b*; the two isomeric butyric acids



behave, however, exactly like one another, and yield in addition to a small amount of hexane (II *a*), propylene $\text{CH}_3 \cdot \text{CH} = \text{CH}_2$ (II *b*). Whereas, on the one hand acetic acid reacts to over 90 per cent. according to I *a*, and only to a minute amount according to I *c*, from its direct derivative trichloroacetic acid, scarcely a trace of the very stable hexachlorethane $\text{CCl}_3 \cdot \text{CCl}_3$ (II *a*) is obtained, but a large amount of the trichlormethyl ester of trichloroacetic acid II *c*.

14. ETHANE FROM SODIUM ACETATE.



A cylinder of nickel or copper gauze is placed as cathode

in a beaker and surrounds a porous pot with a platinum spiral or small platinum sheet as anode. A loosely-fitting wide glass tube is cemented with plaster of Paris in the upper quarter of the porous pot, the tube is closed with a rubber stopper which takes the lead for the anode, a glass delivery-tube, and a thermometer. The anode gas passes first through a Geisler potash bulb for separation and weighing of the carbonic acid, and is then collected

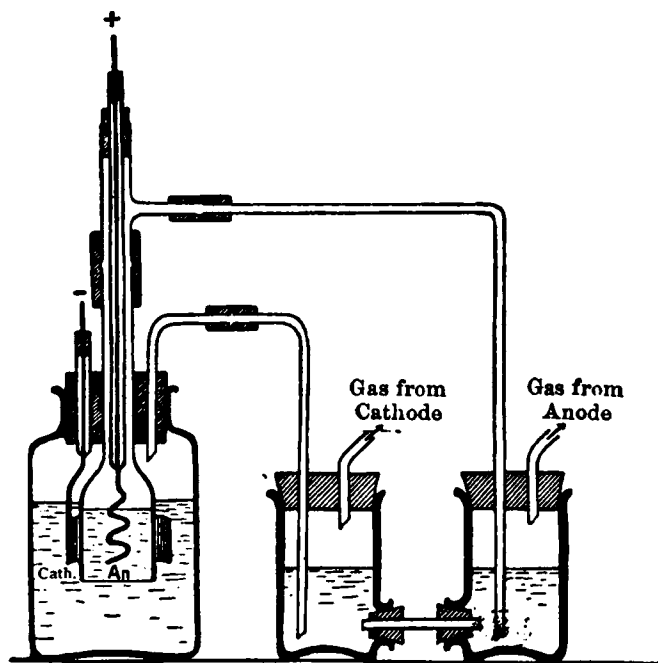


FIG. 8.

over water. The anode and cathode solution is a solution of sodium acetate almost saturated in the cold, which has been acidified with a few cubic centimetres of acetic acid. High current density at the anode is advantageous; it should be at least 50 amperes, still better, over 100 amperes, per 100 sq. cms. (With the arrangement described, the anode is active on both sides.)

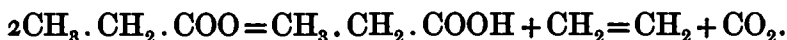
The temperature in the anode chamber must be kept below 20° by good cooling; the current yield of ethane

amounts to about 90 per cent., but sinks already at 30° to 40° to 60 per cent., and at 100° to 1 per cent.

If it is desired to collect the hydrogen and ethane mixed, the porous pot is dispensed with; a wide-necked bottle is used as bath, and through the stopper pass the current leads for anode and cathode, as also a thermometer and gas delivery-tube. The internal resistance is smaller, the heat evolution therefore less, and besides, the cooling is more efficient. However, by a suitable arrangement, the gases from the cathode and anode can be collected separately without employing a porous pot, and since such an apparatus can often be of use, a suitable way of fitting it up is shown in Fig. 8, which will be understood without further description¹.

A disadvantage of this apparatus is the large waste space; it can therefore only be employed in electrolyses of long duration, as otherwise the gases are contaminated by mixture with air.

15. ETHYLENE (ETHYLENE DIBROMIDE) FROM SODIUM PROPIONATE.



A wide-necked bottle contains as electrolyte a solution of 30 grams sodium propionate and 25 grams propionic acid in 80 grams water; a rubber stopper closes the bottle, and through this pass an anode of platinum wire, a cathode of platinum foil, a thermometer, and a gas delivery-tube; the delivery-tube is connected with a wash-bottle containing caustic potash to absorb the carbonic acid, a wider wash-bottle, or better, a Winkler absorption-spiral charged with 15 c.c. bromine and a little water to transform the ethylene into the dibromide, whilst, finally, the gases pass through

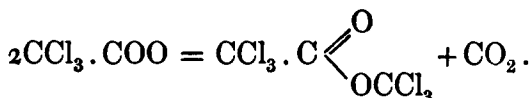
¹ I have adopted the principle of this apparatus from a French publication of Ch. Renard, who suitably calls the arrangement 'Compensateur hydraulique'; the reference and date of the publication I can no longer recollect.—AUTHOR.

a small wash-bottle containing sodium bisulphite or caustic soda solution.

$D_A = 100$ amperes per 100 sq. cms.; D_C unimportant.

The bath and bromine spiral are cooled with water; the temperature of the bath, however, can rise to 40° without harm. After completion of the experiment—15 to 20 ampere hours should be passed through the cell—the contents of the bromine tube are washed with dilute caustic soda, then with water, after which they are dried with fused calcium chloride and then distilled; the fraction of the ethylene dibromide which passes over between 127° and 132° is collected and weighed. The current yield of ethylene varies between 36 and 54 per cent. With the hydrogen there escapes from the last wash-bottle *n*-butane, which only amounts to a few per cent. (0.5 to 10).

16. TRICHLORMETHYL ESTER OF TRICHLORACETIC ACID FROM A MIXTURE OF SODIUM AND ZINC SALTS OF TRICHLORACETIC ACID.



Cathode liquid: Solution of common salt.

Anode liquid: 30 grams trichloroacetic acid, dissolved in 100 grams water, and saturated with a mixture of equal parts by weight of anhydrous sodium carbonate and zinc carbonate.

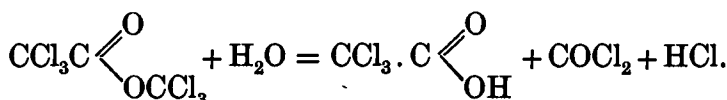
Bath: A beaker with porous pot containing a platinum sheet as anode, and surrounded by a cylindrical cathode of platinum or lead.

$D_A = 40$ –50 amperes per 100 sq. cms.; D_C unimportant.

Current strength: 2 to 4 amperes. Good cooling, preferably with iced water, is necessary.

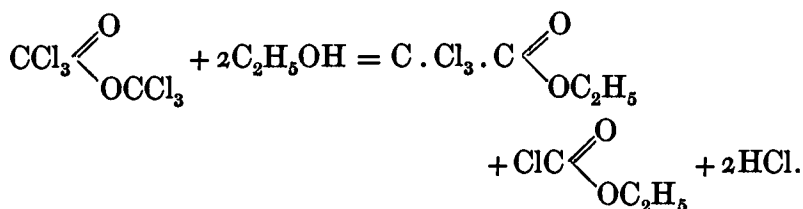
From time to time, at intervals of a quarter of an hour, the electrolysis is interrupted; the ester which has separated as a white crystalline crust upon the anode and at the

bottom of the porous pot is filtered off and dried upon porous plates. After three or four such electrolyses the anode liquid will have become useless; it is, however, more suitable for cathode liquid than the solution of common salt, in case the experiment is continued. The current yield of ester amounts to 10–30 per cent. of the theoretical. The trichlormethyl ester of trichloroacetic acid melts at 34 degrees. It is insoluble in water, but is rapidly decomposed.

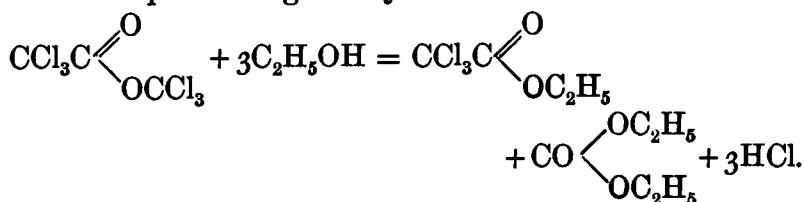


Since it is always moist from its preparation and cannot be quite freed from water, and moreover cannot be dried by the usual drying methods, because the decomposition proceeds more rapidly than the drying, one cannot preserve this substance. The ester can be rapidly freed from the greater part of the adhering water by dissolving it in petroleum ether or benzene, and pouring the solution through a dry filter; by evaporation of the solvent the ester crystallizes well, but soon decomposes on account of the unavoidable trace of adhering moisture.

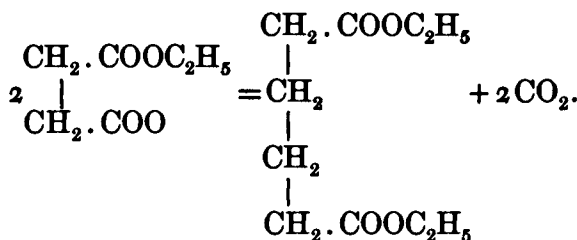
The substance reacts strongly with an ethereal solution of a little absolute alcohol.



By warming with alcohol, the chlorformic acid ether passes over into the ether of carbonic acid, so that in this case the equation is given by:

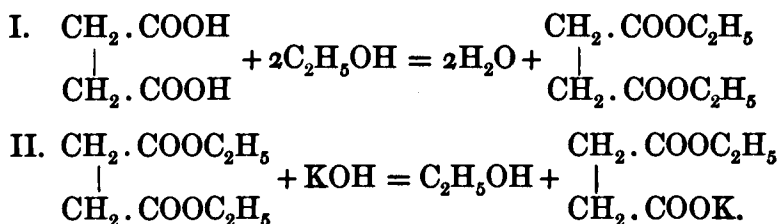


17. THE ETHYL ESTER OF ADIPIC ACID FROM THE POTASSIUM SALT OF THE ETHYL ESTER OF SUCCINIC ACID.



A narrow beaker, which is filled at most to half its height, contains as electrolyte 40–60 c.c. of a concentrated aqueous solution of the potassium salt of the acid ethyl ester of succinic acid (1.5 parts salt to 1 part water), as anode a platinum spiral, as cathode a platinum sheet. $D_A = 50$ to 100 amperes per 100 sq. cms. D_C unimportant. The bath must be well cooled. The somewhat viscous electrolyte froths considerably during the experiment; gases having the odour of melons are given off and the adipic acid ester floats as an oily layer upon the aqueous solution. At least 15 ampere hours are employed; the oil is separated from the solution, washed with water, dried and warmed for some time at 100–110 degrees, whereby it loses its penetrating smell and becomes approximately pure. A complete purification can be effected by fractional distillation in vacuo. The lower boiling fraction contains the ethyl ester of acrylic acid (B.P. 101°). Current yield of adipic acid ester, 30 to 35 per cent.

PREPARATION OF POTASSIUM ETHYL SUCCINATE FROM SUCCINIC ACID.



I. 300 grams succinic acid, 500 c.c. alcohol (96 %) and 20 c.c. concentrated sulphuric acid are warmed together for three hours on a water bath with reflux condenser, and the solution after cooling, poured upon a mixture of 150 grams soda crystals, then separated from the aqueous solution in a separating funnel, quickly washed with a little ice-cold water, dried and distilled, the fraction at 210–220° C. is collected as the diethyl ester of succinic acid. Yield: 90 per cent. of the succinic acid employed.

II. 150 grams of the diethyl succinate are diluted with 100 c.c. alcohol, and mixed with an alcoholic solution of 48 grams caustic potash sticks. The mixture becomes warm and some salt separates; after standing three hours the mixture is evaporated almost to dryness on the water bath, a current of CO₂ being passed through the apparatus; it is then taken up with water (100–150 c.c.), shaken out with a little ether to remove the unaltered diethyl succinate, and finally evaporated down a little. This concentrated solution, contaminated with potassium succinate and potassium carbonate, serves for the electrolysis.

B. ELECTRO-CHEMICAL METHODS OF REDUCTION.

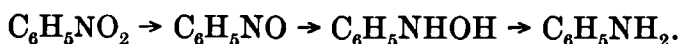
I. Electro-chemical Reduction of Aromatic Nitro-compounds.

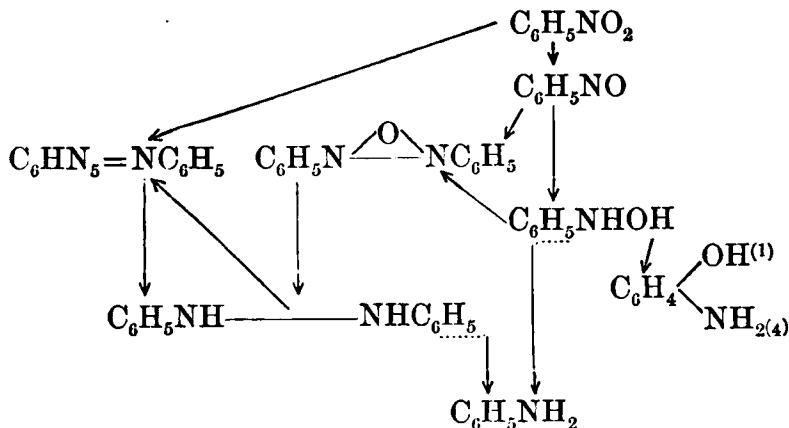
References: K. Elbs, *J. pr.* 43, 39–46 (1891); Haussermann, *Ch. Ztg.* 17, 129, 209 (1893); K. Elbs, *Ch. Ztg.* 17, 209 (1893); L. Gattermann and Koppert, *Ch. Ztg.* 17, 210 (1893); *B.* 26, 2810 (1893); L. Gattermann, *B.* 26, 1844–1856 (1893)*; 27, 1929 (1894); 29, 3034, 3037, 3040 (1896)*; A. A. Noyes and A. A. Clement, *B.* 26, 990–992 (1893)*; A. A. Noyes and Dorrance, *B.* 28, 2349 (1895); K. Elbs, *Z. Elch.* 2, 472–475; 4, 87–88; *Ch. Ztg.* 22, 332 (1898); *Z. Elch.* 7, 119–120, 133–138*, 141–146*; *Z. ang. Ch.*

1899, 389-392; K. Elbs and O. Kopp, *Z. Elch.* 5, 108-110; K. Elbs and R. Illig, *Z. Elch.* 5, 111-113; K. Elbs and B. Schwarz, *Z. Elch.* 5, 113-115; *J. pr.* 63, 562-568 (1901); A. Rhode, *Z. Elch.* 5, 322-324; 7, 328-332; 338-341; K. Elbs and F. Silbermann, *Z. Elch.* 7, 589-591*; A. Chilesotti, *Z. Elch.* 7, 768-773*; Haeusserrmann, *Z. ang. Ch.* (1901), 380; W. Löb, *Z. Elch.* 2, 529-533; 3, 45-48, 471; 4, 428-437; 5, 456-462; 7, 320-328, 333-338*; *Z. ang. Ch.* 1896, 239, *Z. ph. Ch.* 34, 641-668 (1900); B. 29, 1390, 1894 (1896); 31, 2201 (1898); Kauffmann and Hof, *Ch. Ztg.* 20, 542 (1896); F. Haber, *Z. Elch.* 4, 506-513*, *Z. ang. Ch.* (1900), 433-439; F. Haber and Schmidt, *Z. ph. Ch.* 32, 271-287 (1900)*, *Z. Elch.* Ref. 6, 512; Farbenfabriken vorm. F. Bayer und Co., *D. R. P.* Nos. 75,260, 105,501; Straub, *D. R. P.* No. 79,731; Anilinölfabrik A. Wülfig, *D. R. P.* Nos. 100,233; 100,234*, 108,427*; W. Löb, *D. R. P.* Nos. 99,312, 100,610, 116,467; C. F. Boehringer und Söhne and C. Messinger, *D. R. P.* No. 109,051; Chemische Fabriken vorm. Weiler-ter-Meer, *D. R. P.* No. 116,871; C. F. Boehringer und Söhne, *D. R. P.* Nos. 116,942*, 117,007*.

A general view of the wide field of the electrochemical (and chemical) reduction of aromatic mononitro compounds can be best obtained from the diagram, which F. Haber has produced from the results of his own experiments and those of previous workers to represent the process of reduction of nitrobenzene. Numerous independent researches have proved that this scheme can be applied to any other aromatic mononitro compounds, and may therefore be generally accepted. This, of course, must not be understood as though the reduction products of other nitro compounds correspond in quantitative or even in qualitative manner with those of nitrobenzene. Upon the foundation of Haber's scheme, however, we are in a position to determine either directly or from specially planned experiments what are the causes of variation in particular cases. The diagram which is here reproduced represents all the important processes in the reduction of nitrobenzene. (The vertical arrows represent electrochemical reductions, the oblique arrows, on the other hand, purely chemical changes.)

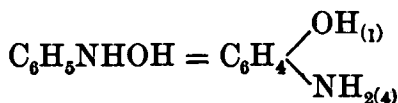
The primary reduction products starting from nitrobenzene are therefore—nitrosobenzene, phenylhydroxylamine, aniline.



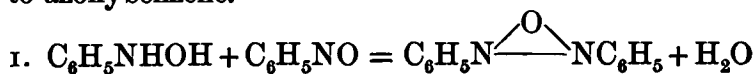


Nitrosobenzene is still more easily reduced than nitrobenzene, and is, therefore, rapidly converted into phenylhydroxylamine; this is fairly stable in moderately acid solution and is further reduced to aniline. Thus by powerful reduction in moderately acid solution the amido group is obtained from the nitro group, from the nitro compound the corresponding amine, without easily separable intermediate productions. (Example No. 18.)

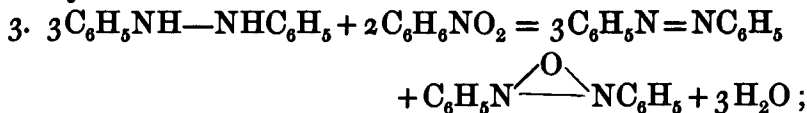
If the solution is very strongly acid, then the purely chemical transformation of the phenylhydroxylamine to the isomeric *p*-amidophenol occurs with considerable velocity:



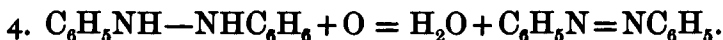
which is not capable of further reduction (Example No. 19). To what extent aniline is formed at the same time by the direct reduction of phenylhydroxylamine before it suffers the tautomeric change, depends on the experimental conditions. If the solution is alkaline, then two new reactions occur leading from the phenylhydroxylamine to azoxybenzene.



The interaction between phenylhydroxylamine and nitrosobenzene (1), in presence of free alkali, occurs so quickly that the phenylhydroxylamine, which is only slowly reducible, does not come into further consideration, whereby the reduction is quite transferred from the direction leading to amine, to that leading to the azo series. The equation (2) is fulfilled only to quite a small extent. Azoxybenzene now takes the place of phenylhydroxylamine as a point of attack for further reduction, and is reduced to hydrazobenzene. This is the secondary reduction process which generally stops here, since hydrazobenzene is only very slowly reduced further to aniline. Hydrazobenzene is, however, a substance, which so long as any nitrobenzene is still present, interacts quickly with it to form azobenzene and azoxybenzene.

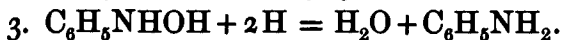
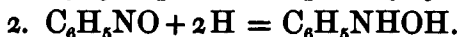
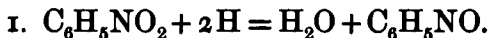


and besides, in presence of alkali, is rapidly oxidized by the oxygen of the air to azobenzene.



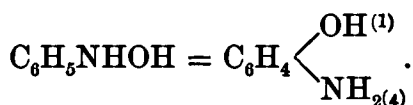
Both reactions are the source of azobenzene, which is neither a direct nor an indirect reduction product, and to their combined action is to be credited the fact that, by suitable conditions of working, excellent yields of azobenzene can be easily obtained. With nitrobenzene as an example, the scheme of the progress of reduction of an aromatic nitro-compound can be expressed by equations as follows:—

I. *Reduction in moderately acid solutions.* Series of primary reduction products, of which usually only the last can be easily separated.

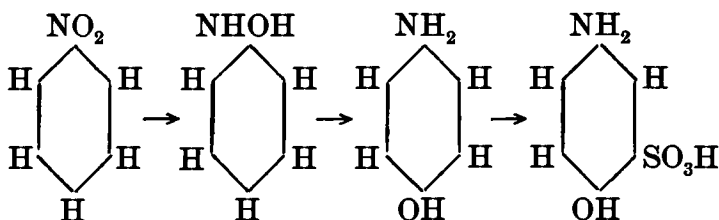


(Example No. 18.)

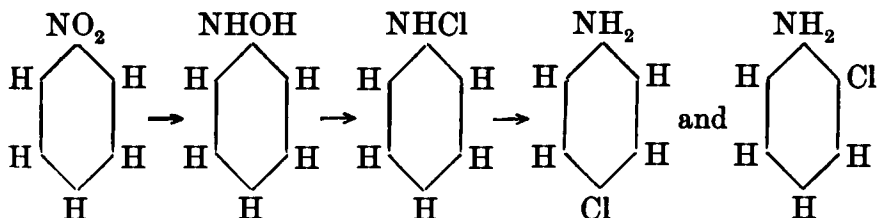
II. *Reduction in strongly acid solution.* The two equations I, 1 and 2, are in the main alone fulfilled, since the transformation of phenylhydroxylamine into *p*-amidophenol, which occurs quickly under the action of strong acids, gives a substance which is not further reducible and thus remains as the final product.



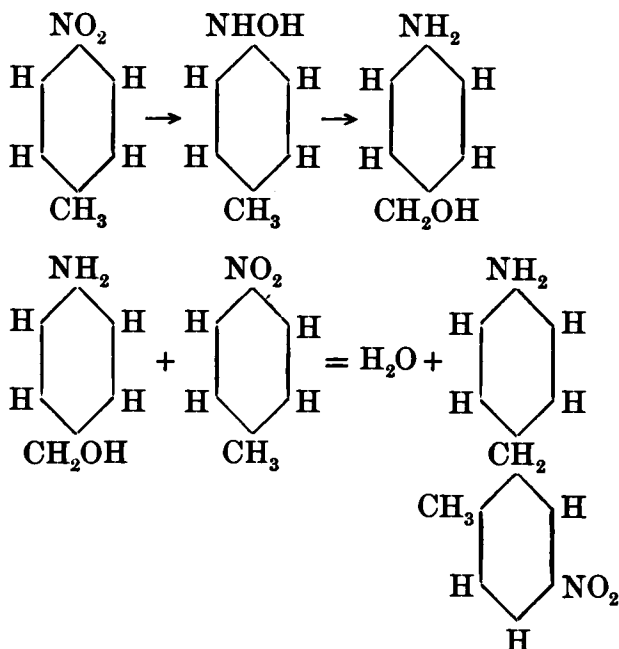
This tautomeric change is, however, in general only possible, if the *p*- or *o*- position to the original nitro-group is free, and even then secondary reactions often occur under the influence of the acids. Thus, from nitrobenzene in sulphuric acid, *p*-amidophenol and by simultaneous sulphonation *p*-amidophenol-*o*-sulphonic acid (Examples 19 and 20) is produced.



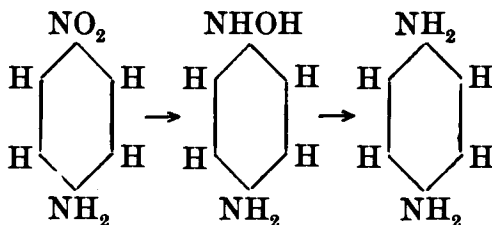
or, in hydrochloric acid, *p*-chloraniline and *o*-chloraniline :



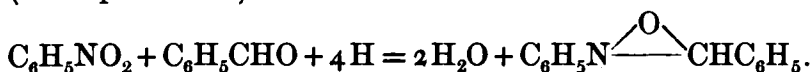
With *p*-nitrotoluene (*p*-tolylhydroxylamine), one H atom of the methyl group changes place with the OH, and consequently *p*-amidobenzylalcohol is formed, which in presence of strong sulphuric condenses with still unaltered *p*-nitrotoluene to *p*-amidophenyl-*m*-nitro-*o*-tolymethane.



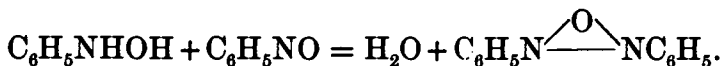
If no tautomeric change occur, then the hydroxylamines are reduced normally to amines.



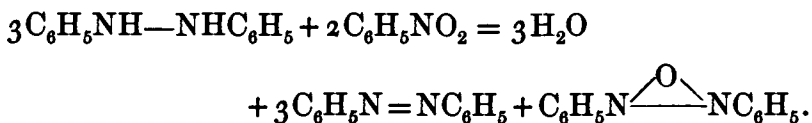
By suitable condensation during the experiment, the transformation of hydroxylamine can be prevented, and a sure proof obtained that the amidophenols are secondary transformation products of previously formed hydroxylamines; thus, by the electrical reduction of nitrobenzene in presence of benzaldehyde, benzylidene phenylhydroxylamine is produced, which is stable under the conditions of the experiment, and can thus be obtained without difficulty (Example No. 21).



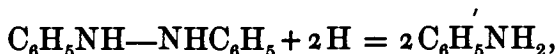
III. *In alkaline solution*, the two equations I, 1 and 2, are fulfilled, just as in acid, nitroso-compounds and hydroxylamine are produced; these are, however, withdrawn from further reduction by the quickly occurring condensation to azoxybenzene, chiefly according to the equation:



Whilst now further quantities of nitrosobenzene and phenylhydroxylamine are being produced by reduction, and are transformed by condensation to azoxybenzene, this latter also suffers reduction to hydrazobenzene; however, this product cannot increase in quantity so long as nitrobenzene is present in the electrolyte, for it is oxidized continuously by the nitro-compound to azobenzene and azoxybenzene, as expressed by the equation:

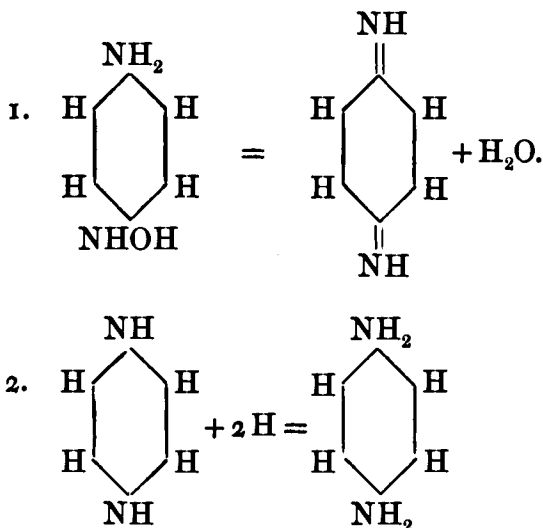


Azobenzene is subject to no further transformation, and is also only slowly reduced to hydrazobenzene; the latter is, however, rapidly oxidized back to azobenzene by the oxygen of the air in alkaline solution, so that azobenzene, and azo-compounds generally, can be obtained easily with excellent yields. This does not hold as a rule for azoxybenzene; the electrolytic reduction is suitable for the production of azoxy-compounds only under special conditions, which indeed is clear from the above. (Examples: Azo-compounds, Nos. 26, 27, 28; azoxy-compounds, Nos. 22, 23, 24, and 25.) Hydrazobenzene, however, since it is only very slowly reduced according to the equation:

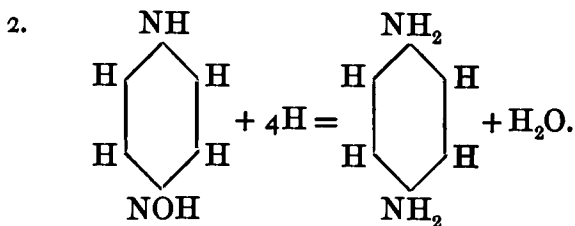
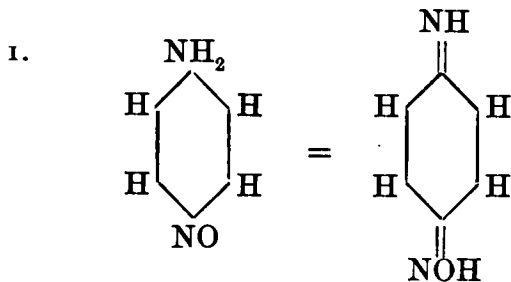


and after the disappearance of the nitro-compound is also subject to no further chemical attack, is the final product of the electrolytic reduction in alkaline solution, and there-

fore easily and satisfactorily prepared. (Examples: Nos. 29, 30, and 31.) According to the above, the electrochemical reduction in alkaline solution gives a general preparation method for the azo- and hydrazo-compounds, on the other hand, only in particular cases, for the azoxy-compounds. A number of observations on the electrolytic reduction in alkaline solution seem to contradict the statement made at the commencement, that the scheme and the explanations given with it hold without exception. The explanation of these particular cases offers, however, no difficulties. In some special cases amines are formed instead of azo-compounds; thus, under identical experimental conditions *m*-nitraniline yields *m*-diamido-azobenzene, *p*-nitraniline, however, *p*-phenylenediamine; this difference rests upon the fact that *p*-nitraniline easily yields quinone derivatives, which the *m*-nitraniline does not. If *p*-nitraniline is reduced to *p*-nitro-phenylhydroxylamine, then this is transformed into quinone diimide, which then by further reduction can only yield diamine:

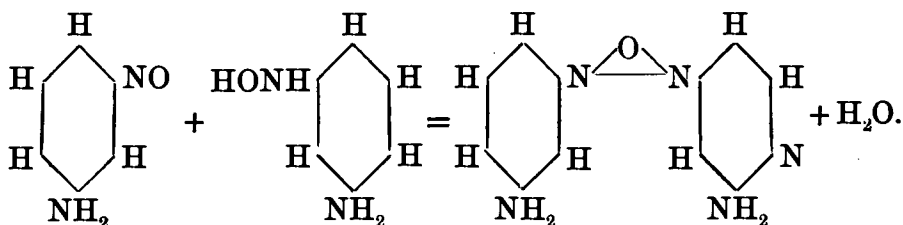


The method of explanation is not at all altered if a similar transformation is supposed to occur in the previous reduction stage, that of the nitroso-compound:

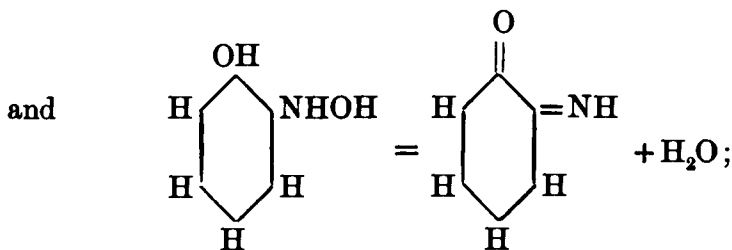
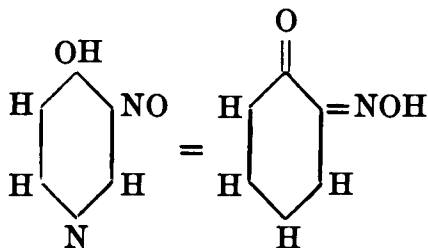


For the quinoneimidoxime by further reduction can only lead to *p*-phenylenediamine.

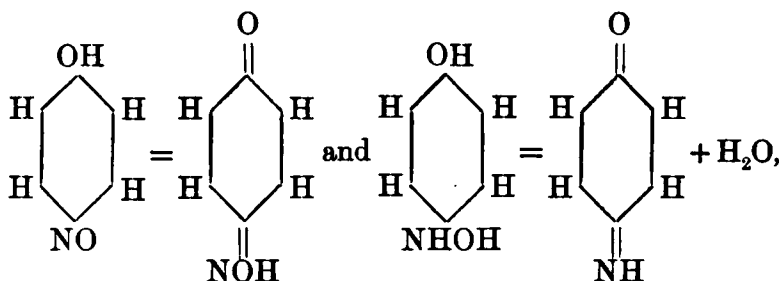
The case is different with *m*-nitraniline, by which as *m*-di-substitution product the tendency to formation of quinone derivatives is altogether wanting. Here the nitroso and hydroxylamine derivatives react easily together and produce the azoxy derivative, whereby the process of reduction is led over into the azo series:



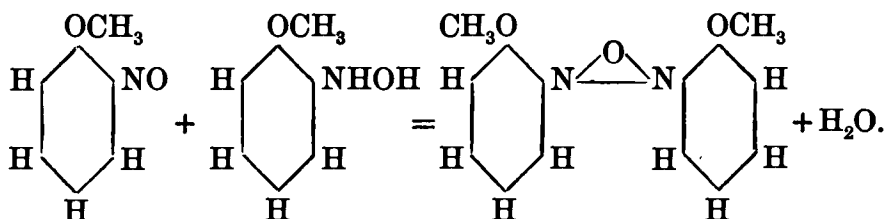
Another example: *o*- and *p*-nitrophenol yield *o*- and *p*-amidophenol; *o*- and *p*-nitroanisole, on the other hand, the corresponding azo compounds. From the two nitrophenols in point of fact quinone derivatives are produced:



or, on the other hand,

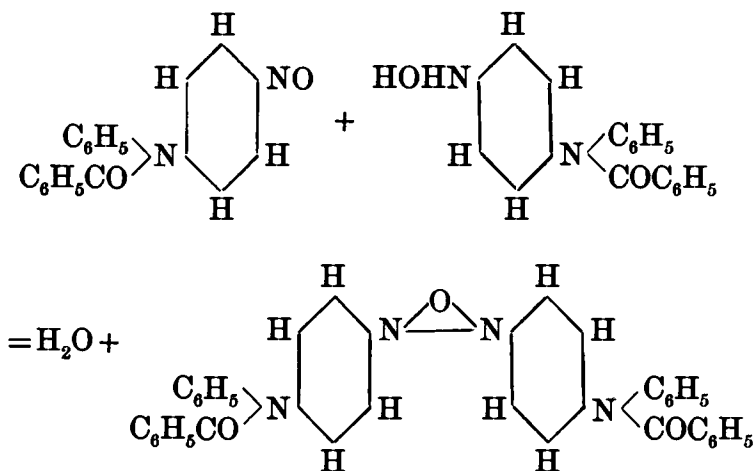


which are further reduced to amidophenols. If, however, the phenol hydroxyl group is etherified, then the formation of quinone derivatives is hindered, and the reduction is led over to the azo series by the reaction between nitroso and hydroxylamine derivatives.

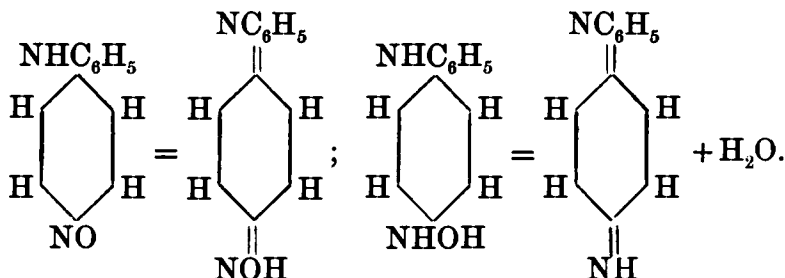


The same holds if in an *o*- or *p*- nitro amine, the amido group is acylized; not, however, if it is alkylized¹.

Thus *p*-nitrobenzoyldiphenylamine yields azo derivatives, because its nitroso and hydroxylamine compounds cannot change tautomerically to quinone derivatives, but condense to benzoylazoxydiphenylamine.



p-Nitrodiphenylamine, on the other hand, yields *p*-amido-diphenylamine, because here nothing stands in the way of the formation of quinone derivatives:

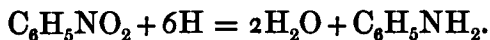


(Examples Nos. 32 and 33.)

¹ Quaternary ammonium compounds should behave as acylized amines; an experimental proof of this is still required, since it has not yet been possible to prepare a nitro-ammonium compound suitable for investigation.

i. *Reduction in moderately Acid Solution ; preparation of Amines.*

18. ANILINE FROM NITROBENZENE.



Bath: A slender beaker, in which a porous pot serves as anode chamber, and the narrow space between the porous cell and the walls of the beaker as cathode chamber; the upper third of the beaker remains empty and acts as a condenser for the alcohol vapours.

Anode liquid: Dilute sulphuric acid of 1.1 sp. gr.

Cathode liquid: 20 grams nitrobenzene, 150 c.c. alcohol, 125 c.c. dilute sulphuric acid of 1.2 sp. gr.

Anode: Sheet-lead.

Cathode: Lead cylinder 20 x 25 cms. with stamped out holes.

D_A : unimportant; $D_C = 3$ to 6 amperes per 100 sq. cms.

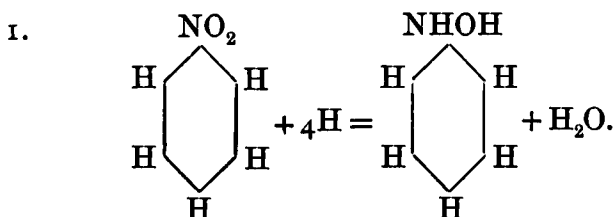
The electrolyte is filled in whilst warm; by the high current-strength and concentration (15 to 30 amperes to 300 c.c. cathode liquid, thus, current-concentration = current-strength to 1 litre solution = 50-100 amperes) the solution soon reaches the boiling-point: after passage of 26 to 27 ampere hours the reduction is complete. By titration of a sample with sodium nitrite, a current efficiency of more than 90 per cent. is determined. The alcohol is distilled off from the cathode liquid, and the solution, if necessary, evaporated somewhat; then by slowly cooling 19.5 to 20.5 grams aniline sulphate are obtained, corresponding to a yield of material of 86 to 87 per cent. A new lead cathode requires first to have a coating of spongy lead, which is best effected by the method given on page 90. *o*-Nitrotoluene similarly reduced is transformed to at least 90 per cent. into *o*-toluidine; if the solution is made alkaline and the free base distilled off, 75 to 85 per cent. of the calculated amount of pure *o*-toluidine can be obtained. *m*-Nitrotoluene shows quantitatively the same

behaviour as the *o*-compound; with *p*-nitrotoluene the yields of *p*-toluidine are generally some per cent. lower. The progress of the reduction is clear from the previous explanations; it only remains to note that in moderately acid solution phenylhydroxylamine is not only subject to reduction, but undergoes also two purely chemical changes, which lower the yield of aniline and produce by-products. Firstly, the molecular transformation to *p*-amidophenol, which is the chief reaction in presence of concentrated acids, progresses slowly even in moderately acid solution; secondly, the condensation between phenylhydroxylamine and nitrosobenzene, which is the characteristic of the alkaline solution, proceeds with a small velocity in weak acid solutions also, whereby azoxybenzene and benzidine are produced by molecular transformation of hydrazobenzene.

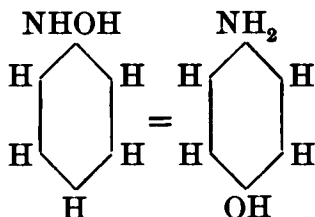
The reduction of phenylhydroxylamine has thus to compete with two chemical reactions; these are subordinated as much as possible by rapid and powerful reduction. For this purpose, lead is to be recommended for cathode material, firstly because, on account of the over-voltage, it takes a very low cathode potential; this fact, however, is not of the greatest moment. Still more important is the formation of a layer of spongy lead, whereby the real active surface is rendered enormously greater than the geometrically measured surface. Tin is just as suitable as lead, because although it possesses no considerable cathodic over-voltage, yet it shows to a high degree the tendency to form spongy metal.

ii. *Reduction in strong Acid Solutions; preparation of Hydroxylamine Derivatives.*

19. *p*-AMIDOPHENOL FROM NITROBENZENE.



2.



Bath: Beaker with porous pot as cathode chamber.

Anode liquid: Ordinary concentrated sulphuric acid mixed with a little water.

Cathode liquid: Solution of 20 gms. $\text{C}_6\text{H}_5\text{NO}_2$ in 150 gms. pure concentrated sulphuric acid, mixed with a few drops of water.

The porous pot must be completely saturated with the anode liquid before the cathode solution is poured into it.

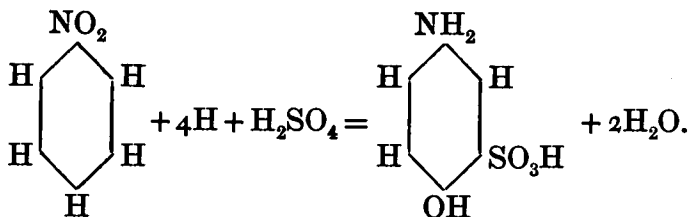
Anode: Sheet of platinum.

Cathode: Wire-gauze or sheet of platinum.

$D_A = D_C = 4$ to 6 amperes per 100 sq. cms.

Warming to 60–90° C. and occasional stirring favour the satisfactory progress of the reaction; about double the theoretical amount of current must be passed. The deep blue coloured contents of the porous pot are poured out into a beaker whilst still hot, the liquid solidifies in a cool place to a dark blue paste of crude *p*-amidophenol sulphate, which is filtered through asbestos at the filter-pump and, without washing, is re-crystallized from hot dilute alcohol. Reckoned from the nitrobenzene the yields vary from 20 to 50 per cent. of the theory; as chief by-products, aniline, *p*-amidophenol, sulphonic acid, and colouring matters are found. The aniline remains as sulphate in the mother-liquor which is drawn off by the pump; the sulphonic acid does not go into solution in the alcohol in the re-crystallization of the impure sulphate. It can be easily obtained by boiling the residue with soda solution and precipitating the hot filtrate with hydrochloric acid.

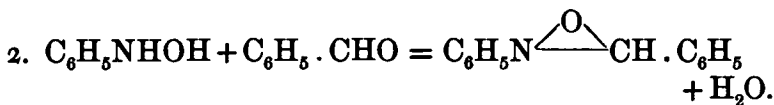
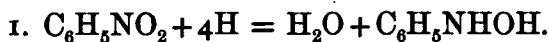
20. *p*-AMIDOPHENOLSULPHONIC ACID FROM
NITROBENZENE.



Bath and electrodes as in previous experiments.

As anode liquid ordinary concentrated sulphuric acid is employed, as cathode liquid a solution of 40 grams $\text{C}_6\text{H}_5\text{NO}_2$ in 150 grams slightly fuming sulphuric acid (sp. gr. 1.86 to 1.88). In proportion as the bath heats up, owing to the progress of the experiment, the current density is increased from 2 to 6 amperes per 100 sq. cms.; during the time that the reaction is in full progress the temperature should not be below 80° nor above 120° . In order to hinder a too large increase of the resistance of the cell, some sodium sulphate solution is carefully added from time to time to the anode acid which has become fuming by the migration of the HSO_4 ions. To obtain complete reduction only about 20 per cent. more current than the theoretical need be passed. When the experiment is finished, the cathode liquid is cooled and poured into three times its volume of water; after several hours standing it is filtered. The filtrate contains aniline and *p*-amidophenol as sulphates, but it is not worth while to recover them; the residue is extracted with hot dilute sodium carbonate solution. From the quickly filtered solution of the sodium salt of the sulphonic acid, the free *p*-amidophenolsulphonic acid is separated as a pale violet, glistening, crystalline powder by immediately acidifying with hydrochloric acid; it is filtered off when quite cold, washed with water, and is then practically pure; it can, however, be easily purified by recrystallization from boiling water. About 40 per cent. of the amount calculated from the nitrobenzene is obtained.

21. BENZYLIDENE PHENYLHYDROXYLAMINE FROM NITRO-BENZENE AND BENZALDEHYDE.



Bath and electrodes as in Example No. 19.

Anode liquid: Mixture of 3 volumes sulphuric acid and 1 volume water.

Cathode liquid: Solution of 18 gms. $\text{C}_6\text{H}_5\text{NO}_2$ and 20 gms. $\text{C}_6\text{H}_5\text{CHO}$ in 40 gms. glacial acetic acid, mixed with 40 gms. concentrated sulphuric acid.

$D_A = D_C = 4$ to 6 amperes per 100 sq. cms. With a current of 1.5 to 2 amperes the electrolysis lasts twenty hours, if a complete reaction is desired; however, a satisfactory yield can be obtained in a much shorter time. During the experiment, the bath is cooled from the outside with water; after completion of the experiment the contents of the cathode chamber are poured into cold water, or better, upon ice, the red crystalline mass which separates out is washed with water and re-crystallized from alcohol, whereby almost pure white crystals of M.P. 108 to 109° C. are obtained. Yield of benzylidene phenylhydroxylamine 26 gms. The essential difference in the reductions in series II from those in I lies in the fact that the strong cathode acid accelerates the purely chemical changes of phenylhydroxylamine; in Examples Nos. 19 and 20 the molecular transformation, in No. 21 the condensation with benzaldehyde. At the same time by weakening and retarding the reduction—low current-concentration and bright platinum electrodes in place of spongy lead—the transformation to amine is hindered. Since under the experimental conditions in all three examples, the hydroxylamine derivatives were neither further reduced nor subject to other chemical changes, they are collected as the final products.

iii. *Reduction in Alkaline Solution ; preparation of Compounds and Derivatives of the Azo and Amine Series.*

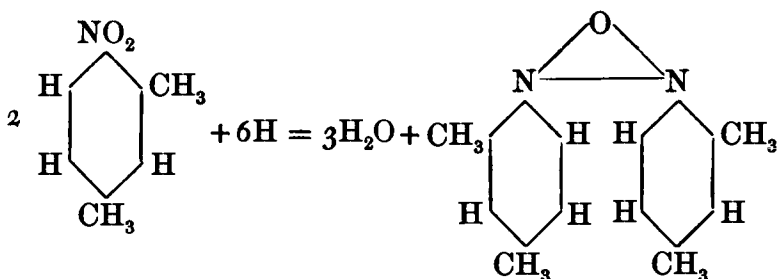
1. Azoxy compounds.
2. Azo compounds.
3. Hydrazo compounds and benzidines.
4. Diamines and amido-phenols.

For all the experiments given in this division, with a single exception, the arrangement of the bath is the same ; consequently it will be described at the commencement. The bottom of a tall narrow beaker is covered with a suitable piece of nickel or copper gauze, which is cut from old useless cathodes and bent into a wavy form around a pencil. Upon this is placed a large porous pot about two-thirds the height of the beaker, and so wide that only a narrow space remains between the beaker and the porous pot. In this space a cylindrical cathode of nickel or copper gauze is placed, whilst in the porous pot a large S-shaped lead plate serves as anode ; in special cases the lead plate is replaced by a lead cooling spiral. Generally, a high temperature is desired, consequently the electrolyte is poured in warm (the cathode solution only after the porous pot has become saturated with the anode liquid) ; after a short time the cathode liquid becomes heated by the current to the boiling point ; the upper empty third of the beaker then acts as condenser. Its efficiency is considerably increased if around this upper third a bandage of felt is fixed, which is kept moist by spraying water upon it ; if, despite these precautions, too much alcohol is lost, then some must be added to make up for the loss. Occasional stirring by sudden raising and sinking of the cathode acts favourably. The current density to be employed varies considerably according to the nature of the material to be treated and the desired stage of reduction ; without exception, however, as short a duration and thus as high a current-concentration as possible is to be desired and is easily attained ; for instance, a current-concentration of 200

amperes even with a moderate current density of 10 amperes per 100 sq. cms. Regulating resistances are almost always unnecessary where a properly graded voltage is available. Whether gauze of nickel or copper is chosen is often of no moment; it is found, however, that disturbing influences make themselves felt more easily with copper than with nickel.

1. Azoxy Compounds.

22. AZOXY-*m*-XYLENE FROM NITRO-*m*-XYLENE.



Anode liquid: Cold saturated sodium carbonate solution.

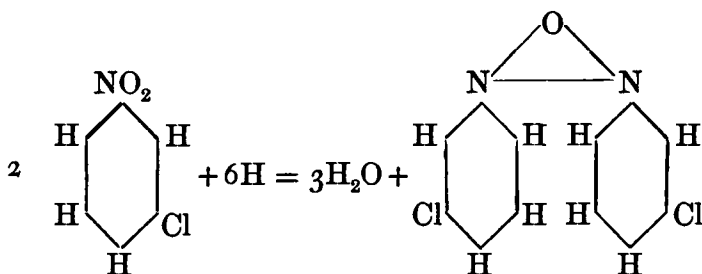
Cathode liquid: 10 gms. nitro-*m*-xylene, 5 gms. crystallized sodium acetate, 100 c.c. alcohol (96 per cent.), 10 c.c. water.

D_c : 1 to 2 amperes per 100 sq. cms. Amount of current, 5.3 ampere hours. Current-efficiency almost quantitative; yield of material 85 per cent. of theoretical.

After completion of the experiment the cathode liquid is allowed to stand in the cold; in this way the azoxy compound separates as a cake of crystalline material. This is filtered off at the pump, washed, and re-crystallized from petroleum ether; it is thus obtained chemically pure in long prisms of a reddish-yellow colour melting at 74°C . By steam distillation of the original mother-liquor, which was filtered off, about $\frac{3}{4}$ gram unaltered nitro-*m*-xylene are obtained in the distillate, and about $\frac{1}{2}$ gram azo-*m*-xylene in the residue. The following are the details entered for an experiment carried out without regulating resistance according to the above instructions.

Time.	Amperes.	Mean Current in amperes.	Ampere minutes.	Remarks.
3.40	2			Solution light yellow.
3.50	4	3	30	Solution reddish yellow.
4	6	5	50	Solution boils.
4.20	6	6	120	
4.40	4	5	100	Slight turbidity, disappearing on addition of a few drops of alcohol.
4.45	4	4	20	
			320 = 5.3 ampere hours	Solution red and clear. From start to finish no evolution of hydrogen.

23. *m*-DICHLORAZOXYBENZENE FROM *m*-CHLORNITROBENZENE.

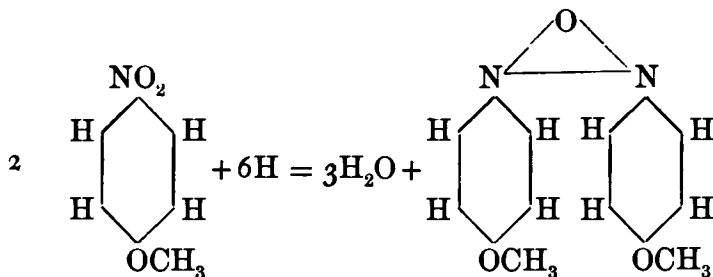


Anode liquid: Cold saturated solution of sodium carbonate.

Cathode liquid: 10 gms. *m*-chlornitrobenzene, 5 gms. crystallized sodium acetate, 200 c.c. alcohol (75 per cent.).

D_C : 1 to 5 amperes per 100 sq. cms.

The cathode liquid is allowed to boil and the current is broken rather before the theoretical amount of current, 5.1 ampere hours, has been passed, at about, say, 5.0 ampere hours. Already during the experiment the difficultly soluble azoxy compound separates in large amount in bright orange crystalline plates. The solution is allowed to cool, filtered off, and re-crystallized from boiling alcohol; a yield of 85 per cent. theoretical of pure *m*-dichlor-azoxybenzene melting at 97° is obtained.

24. *p*-AZOXYANISOL FROM *p*-NITROANISOL.

Anode liquid: Sodium carbonate solution.

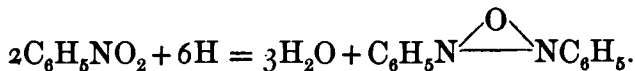
Cathode liquid: 10 gms. *p*-nitroanisol, 2 gms. crystallized sodium acetate, 140 c.c. alcohol (70 per cent.).

D_c : up to 11 amperes per 100 sq. cms.

The electrolysis is carried out at the boiling-point until 5 ampere hours have been passed. The difficultly soluble azoxyanisol separates out in large amount during the experiment. After cooling, it is filtered off at the pump, and the raw product re-crystallized from alcohol. Yellow needles melting at 116° are obtained. Yield of material over 80 per cent. of the calculated amount.

100 parts 96 per cent. alcohol dissolve 0.5 parts *p*-azoxyanisol at 20° , 3.5 parts at 79° .

25. AZOXYBENZENE FROM NITROBENZENE.



The nitrobenzene is reduced as an emulsion and not in the dissolved state, consequently the arrangement of the cell differs from the general form mentioned above. The beaker forms the anode chamber, and has a platinum or lead sheet as anode; the porous pot contains a cylinder of nickel gauze as cathode, and in the middle a powerful stirrer.

Anode liquid: Sodium sulphate solution, acidified with a little sulphuric acid.

Cathode liquid: 30 gms. nitrobenzene, 240 gms. 2.5 per cent. caustic soda solution.

D_c : 5 to 7 amperes per 100 sq. cms.

After passage of 20 to 21 ampere hours the experiment is stopped; already at about 19 ampere hours a gradually increasing evolution of hydrogen will have commenced. The stirrer must work with sufficient power to preserve permanently a uniform emulsion of the cathode liquid. The contents of the porous pot are poured out into a flask and distilled for half an hour with steam; in this way, besides nitrobenzene and aniline, noticeable amounts of azoxybenzene are also carried over; the residual oil solidifies after washing with cold water, and is re-crystallized from petroleum ether. Yield of pure azoxybenzene over 60 per cent.

Of the four azoxy compounds chosen as examples three, namely, azoxy-*m*-xylene, *m*-dichlorazoxybenzene, and *p*-azoxyanisol, are less easily reducible to hydrazo compounds than usual, so that it is possible, if low current densities are employed, whilst passing a quantity of current fully sufficient for the reduction to the azoxy stage, to hinder a further reduction to the hydrazo stage, and thus also the formation of azo compounds. With *m*-dichlorazoxybenzene and *p*-azoxyanisol the fact that both compounds are very slightly soluble in the electrolyte is also of assistance, since they are separated to a considerable extent in a crystalline state during the experiment, and are thus removed from further reduction; in this way it is very easy to obtain good yields of both these azoxy compounds. Such favourable conditions are not present in the case of azoxybenzene, and a satisfactory electro-chemical preparation is only possible by the artifice of employing an emulsion instead of a solution. The very easily reducible nitrobenzene is reduced, even in so unsuitable a condition for reductions; the azoxybenzene, however, as a more difficultly reducible substance, scarcely at all, even when the current exceeds in amount that required by the theory.

2. Azo Compounds.

26. AZOBENZENE FROM NITROBENZENE.



Anode liquid: Cold saturated sodium carbonate solution.

Cathode liquid: 20 gms. nitrobenzene, 5 gms. crystallized sodium acetate, 200 c.c. alcohol (70 per cent.).

$D_C = 6$ to 9 amperes per 100 sq. cms.

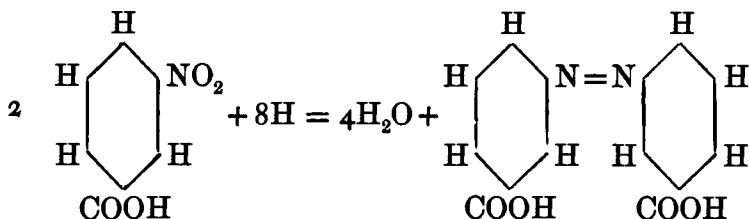
The electrolysis is carried out at the boiling-point; almost exactly to the minute a considerable evolution of hydrogen commences, as soon as the theoretical amount of current (17.4 ampere hours) has been reached; from this point, at a lower current density, 1 to 2 ampere hours more are passed; the hot cathode liquid, which now contains, besides azobenzene, a very little azoxybenzene, not much hydrazobenzene, and no nitrobenzene at all, is poured out into an Erlenmeyer flask, and air is drawn through the liquid for half an hour, in order to oxidize the hydrazobenzene to azobenzene. The greater part of the azobenzene crystallizes out, and can be filtered off nearly chemically pure; the remainder is precipitated by addition of water, or is distilled over in steam; after a single re-crystallization from alcohol or petroleum ether this fraction is also pure. Current-efficiency over 80 per cent.; yield of material over 90 per cent. of the theory.

In the same manner, and with equally good results, the corresponding azo compounds can be obtained from *o*-nitrotoluene, *m*-nitrotoluene, *p*-nitrotoluene, and nitro-*o*-xylene ($(\text{CH}_3)_2\text{C}_6\text{H}_3\text{NO}_2$; indeed the admissible current densities at
(1:2) (4)

the cathode are even somewhat higher. *p*-Hydrazotoluene is not oxidized so easily as most of the other hydrazo compounds, and consequently, in this case, only the amount of current necessary for the formation of *p*-azotoluene is passed through the *p*-nitrotoluene solution. The azoxy-*m*-xylene is more slowly reduced to the hydrazo compounds than its

homologues—upon this peculiarity, as above mentioned, the possibility of its preparation indeed depends—and consequently for the reduction of nitro-*m*-xylene to azo-*m*-xylene, only half the usual current density should be used. As cathode liquid a solution of 10 gms. nitro-*m*-xylene and 5 gms. crystallized sodium acetate in a mixture of 120 c.c. alcohol (96 per cent.) and 20 c.c. water is employed; the current density at the cathode should be 3 to 6 amperes per 100 sq. cms., and the amount of current passed 10 per cent. over the calculated amount. The limit is very sharply defined; as soon as the theoretical amount of current has been passed through the solution, a copious evolution of hydrogen commences. The after treatment of the cathode liquid is identical with that adopted for azobenzene.

27. *m*-AZOBENZOIC ACID FROM *m*-NITROBENZOIC ACID.

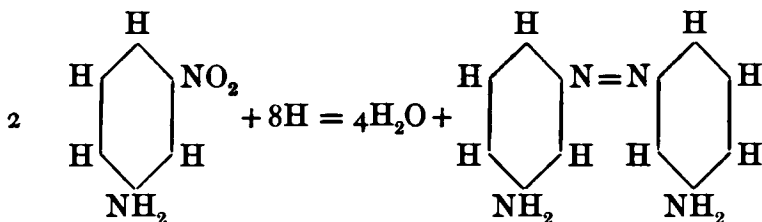


Anode liquid: Sodium carbonate solution.

Cathode liquid: 10 gms. *m*-nitrobenzoic acid are mixed with 100 c.c. water, and just sufficient sodium hydrate solution is added to complete the solution of the acid.

D_c : 4 to 6 amperes per 100 sq. cms.

As soon as the theoretical amount of current has been passed, which is denoted fairly sharply by the commencement of hydrogen evolution, the cathode liquid is poured into a bottle, well shaken with air, the *m*-azobenzoic acid precipitated by hydrochloric acid, filtered at the pump, and washed first with water, then with hot alcohol. The current-efficiency and yield of material are almost quantitative.

28. *m*-DIAMIDOAZOBENZENE FROM *m*-NITRANILINE.

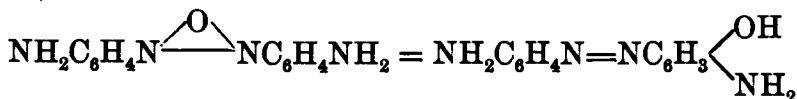
Anode liquid: Sodium carbonate solution.

Cathode liquid: 20 gms. *m*-nitraniline, 5 gms. crystallized sodium acetate, 200 c.c. alcohol (70 per cent.).

D_C : 4 to 8 amperes per 100 sq. cms.

Instead of the theoretical 15.5 ampere hours, 16 to 17 ampere hours are passed through the hot solution; the cathode liquid is allowed to crystallize in the cold, and the remainder of the azo compound is precipitated in a less pure condition from the mother-liquor by pouring it into water; a trace of *m*-phenylenediamine remains in solution. Current-efficiency over 90 per cent.; yield of material over 80 per cent. of the theory. By re-crystallization from dilute alcohol, the *m*-diamidoazobenzene is obtained in fine orange needles which melt at 146 to 148° C. The substance is, however, still contaminated with several per cent. *m*-diamidoazoxybenzene, from which it can scarcely be freed by re-crystallization. With moderate losses the separation can be carried out by treating the impure, quite dry, compound with ten times its weight of pure concentrated sulphuric acid, with which it is heated to 100–110° C. for two hours; the deep brown solution after cooling is poured into five times its volume of water; it is then treated with caustic soda in excess, and the crystalline precipitate is filtered off, washed with caustic soda solution, and then with water, and finally re-crystallized from dilute alcohol; the *m*-diamidoazobenzene is now pure, and melts at 154 to 156 degrees. The *m*-diamidoazoxybenzene present in the raw product is

transformed by this treatment with sulphuric acid into *m*-diamido-oxyazobenzene.



which, as a phenol, dissolves in sodium hydrate, and is thus easily removed.

According to previous considerations the azo compounds are formed very indirectly. The nitro compounds yield, as a first product, a nitroso compound, which is very easily further reducible; as a secondary, more difficultly reducible product, a hydroxylamine; these two condense quickly to an azoxy compound, which suffers reduction to a hydrazo compound. With moderate velocity this then reacts with still unattacked nitro compound to produce the azo compound. So long as nitro compound is still present, high current densities can be employed without evolution of hydrogen occurring at the cathode, and the formation of azo compounds proceeds regularly. With the transformation of the nitro compound, the easily reducible compounds (RNO_2 and RNO) disappear from the electrolyte, and hydrogen is evolved; the azoxy compounds, which are still present at the period, are reduced slowly to hydrazo compounds; the azo compounds suffer the same change, but still more slowly, and in absence of nitro compound only the air is answerable for the oxidation of hydrazo to azo compound. Generally, the evolution of hydrogen occurs almost exactly at the instant when the theoretical amount of current necessary for the production of azo compound has been passed; however, the commencement of the evolution of gas does not denote just that point where only azo compound is present, and the further reduction to hydrazo compound commences, but rather where the nitro compound has altogether disappeared from the solution. The cathode liquid contains at this instant, besides azo compound, some azoxy and hydrazo compounds. Since azoxy and azo compounds are generally difficult to

separate it is usually advantageous, from the commencement of the hydrogen evolution, to pass about 10 per cent. more than the theoretical amount of current at a diminished current density, so that besides the azo compound only the hydrazo is present, which latter is oxidized by the air to azo compound, either directly or by passage of a current of air through the liquid, which reaction is accelerated considerably by the presence of alkali.

3. *Hydrazo Compounds and Benzdines.*

29. HYDRAZOBENZENE AND BENZIDINE FROM NITRO-BENZENE.

1. $2\text{C}_6\text{H}_5\text{NO}_2 + 10\text{H} = 4\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{NH}-\text{NHC}_6\text{H}_5.$
2. $\text{C}_6\text{H}_5\text{NH}-\text{NHC}_6\text{H}_5 = \underset{(4)}{\text{NH}_2\text{C}_6\text{H}_4}-\underset{(1)}{\text{C}_6\text{H}_4}\underset{(4)}{\text{NH}_2}.$

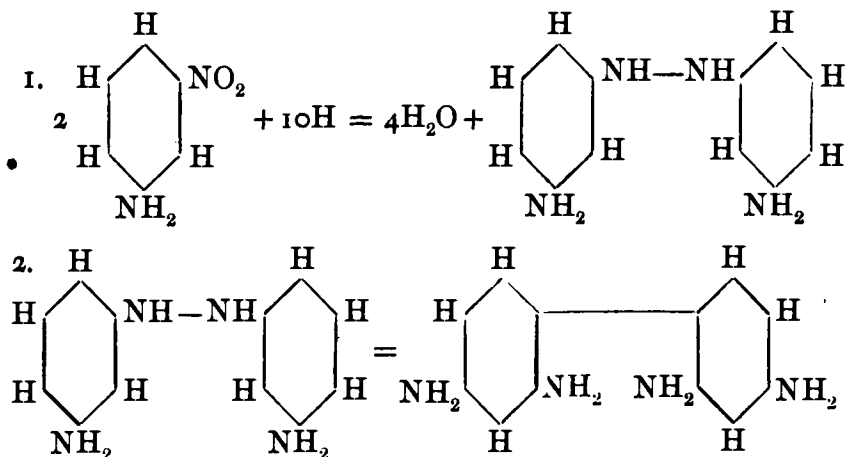
Continuation of Experiment No. 26. After passage of 17.4 ampere hours and commencement of hydrogen evolution, the current density is lowered to $D_c = 1$ to 3 amps. per 100 sq. cms., and 4.4 more amp. hours (the theoretical amount of electricity required) are passed. With very small gas evolution, the deep red cathode liquid becomes lighter in colour; from this point onwards the bath is placed in cold water, and, whilst the hydrazobenzene crystallizes out by the cooling, $\frac{1}{2}$ ampere hour more current is passed at a very low current density. Finally the pasty contents of the cathode chamber are quickly filtered off, washed with dilute acetic acid, then with alcohol, and afterwards with petroleum ether and dried. The filtrate is collected in a large filter flask containing 200 c.c. water and a few drops of ammonium sulphide; in this way a second less pure fraction of hydrazobenzene is precipitated, which is treated as the direct crystalline product. Current-efficiency over 80 per cent.; total yield of material over 90 per cent. of the theory.

For the preparation of benzidine, the cell is not cooled during the passage of the last $\frac{1}{2}$ ampere hour of current;

finally some drops of sodium bisulphite solution are added to the cathode chamber, the contents of which are then syphoned off, without breaking the current, into a dish containing a hot mixture of 200 c.c. concentrated sulphuric acid and 400 c.c. of water. The neutralization of the alkaline liquid and the transformation of hydrazobenzene into benzidine sulphate proceeds, accompanied by violent boiling. After cooling, the powdery crystalline benzidine sulphate is filtered off, and is extracted first with alcohol, then with ether, for the removal of the azobenzene, which is formed despite the quick transformation and the presence of sulphurous acid. Yield about 70 per cent. of the calculated amount of benzidine sulphate. A small increase in the yield can be obtained by carrying out the transformation with hydrochloric instead of sulphuric acid, and then by addition of a saturated solution of sodium sulphate to the boiling solution of benzidine hydrochloride, converting it into benzidine sulphate.

o- and *p*-Hydrazotoluene can be obtained in the same manner and with about the same yield as hydrazobenzene, and *o*-tolidine sulphate in the same way as benzidine sulphate.

30. *m*-DIAMIDOHYDRAZOBENZENE AND *m*-DIAMIDO-BENZIDINE FROM *m*-NITRANILINE.



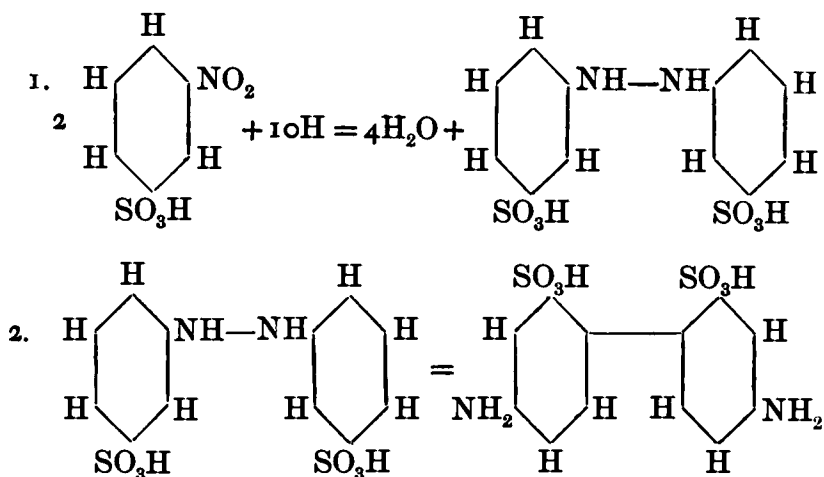
Anode liquid: Sodium carbonate solution.

Cathode liquid: 25 gms. *m*-nitraniline, 5 gms. crystallized sodium acetate, 350 c.c. (96 %) alcohol, 50 c.c. water.

D_c : 6 to 10 amperes per 100 sq. cms. for the formation of the azo compound (current 19.6 amp. hours), 2 to 4 amperes for formation of hydrazo compound (5 amp. hours). From this stage, the bath is cooled and electrolysis continued with $D_c = 0.5$ to 1 ampere per 100 sq. cms., until an excess of about 2 ampere hours have been passed and the cathode liquid has become cold. Accompanied by a considerable evolution of hydrogen, the deep red solution becomes almost colourless, and deposits the hydrazo compound in large amount as a yellowish crystalline powder, which is prevented from adhering to the cathode by raising and lowering this suddenly from time to time. The precipitate is filtered off, washed with water, alcohol, and petroleum ether, and dried in the open air, but not in sunlight. Current-efficiency 75 to 80 per cent.; yield of material 90 per cent. of the theoretical. *m*-Diamidohydrazobenzene is a yellowish sandy crystalline powder, consisting of well-formed strongly refracting crystals, almost insoluble in water, ether, petroleum ether, and benzene; it is difficultly soluble in boiling alcohol and almost insoluble in cold. In the dry state it can be preserved unaltered; it reddens on being heated above 130° and melts, but not sharply, at 152° C. To transform *m*-diamidohydrazobenzene into diamidobenzidine it is dissolved in the necessary amount of glacial acetic acid by warming in a porcelain dish, and as soon as the solution begins to boil, concentrated hydrochloric acid (for the amount produced as above, 40 c.c.) is poured into it. The transformation takes place with frothing, the liquid takes a brownish-violet colour, and when the hydrochloric acid salt of the benzidine begins to separate as a sandy precipitate the flame is removed, and the solution is diluted with double its volume of alcohol and allowed to cool. The precipitate is filtered off, washed with alcohol, and dried in the open air.

The yield of diamidobenzidine hydrochloride amounts to 80 per cent. of the calculated quantity. If the salt is required quite pure, it is dissolved in a little water, filtered, and first hot alcohol, then concentrated hydrochloric acid is added, whereby, after a short time, beautifully formed crystals are obtained.

31. BENZIDINE-*m*-DISULPHONIC ACID FROM *m*-NITRO-BENZENESULPHONIC ACID.



Anode liquid: Sodium carbonate solution.

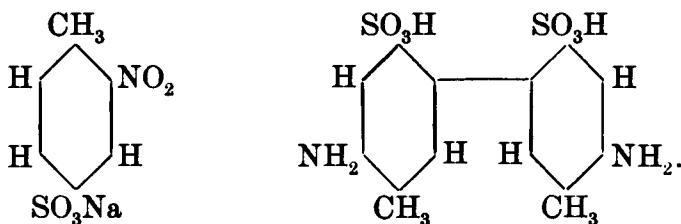
Cathode liquid: 60 gms. sodium *m*-nitrobenzenesulphonate (anhydrous), 350 to 400 c.c. water.

D_c : up to azo stage 3 to 6 amps. per 100 sq. cms., then to the hydrazo stage 0.5 to 1.5 amps., finally about 10 per cent. excess of current with 0.5 amps. per 100 sq. cms. The bath is to be kept the whole time nearly at the boiling-point; during the reduction to the hydrazo stage a small evolution of hydrogen occurs, and in consequence of the great ease with which oxidation by the oxygen of the air occurs, the solution does not become colourless, but remains more or less yellow. The cathode liquid is finally syphoned off, without breaking the current, into a porcelain dish containing a boiling mixture of 250 grams concentrated

sulphuric acid and 500 grams water, and is boiled for a quarter of an hour, until a rich crystalline deposit with red colouration of the solution is obtained. After cooling, the precipitate is filtered off, washed with water, and the contents of the funnel dissolved in hot dilute ammonia; the solution is filtered, and whilst still hot is strongly acidified with concentrated hydrochloric acid. The pure benzidine-*m*-disulphonic acid separates slowly in the cold in well-formed colourless crystals.

Yield: 50 to 60 per cent. of the calculated amount.

According to the same method and with about the same yield, *o*-tolidinedisulphonic acid is prepared from the sodium salt of *o*-nitrotoluenesulphonic acid.



Since accurate descriptions of the preparation of sodium *m*-nitrobenzenesulphonate and sodium *o*-nitrotoluenesulphonate have not been published up to the present, suitable instructions are given in what follows:—

Preparation of Sodium m-nitrobenzenesulphonate.

A mixture of 100 gms. nitrobenzene and 400 gms. ordinary fuming sulphuric acid of 1.9 sp. gr. are slowly heated together in a round-bottomed flask and kept at 150 or 160 degrees for two hours. After cooling, the contents of the flask are poured into 1½ to 2 litres of water and neutralized by sodium carbonate with warming of the solution. Afterwards the liquid is evaporated in a dish until a crystalline crust forms, when it is cooled to 38 degrees and quickly filtered, preferably through a cloth. It is not worth while to work up the mother-liquor. The crystals consist mostly of the sodium sulphonate, to a small extent of sodium sulphate. For the separation, the crystals are extracted several times by boiling with alcohol; the alcoholic solution yields the sulphonic acid salt in brilliant white crystals. The residue, which is apparently insoluble in alcohol, dissolved in a small quantity of hot water, filtered, and evaporated to the crystallizing point, yields still a considerable amount of the sulphonic acid salt. Mean yield of *m*-nitrobenzenesulphonate 70 per cent. of the theoretical.

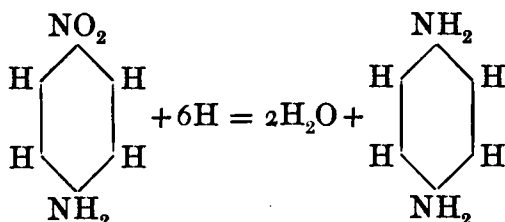
Preparation of Sodium o-nitrotoluenesulphonate.

A mixture of 100 gms. *o*-nitrotoluene and 300 gms. ordinary fuming sulphuric acid is heated in a round-bottomed flask for five hours in a bath of a boiling saturated solution of common salt. After cooling the contents of the flask are poured into 1½ to 2 litres of water, and afterwards submitted to the same treatment as the nitrobenzenesulphonic acid. Yield over 90 per cent. of the calculated amount of sodium *o*-nitrotoluenesulphonic acid.

The earlier theoretical considerations, as also the methods for the formation of azo compounds which have been described, show that, in the electro-chemical reduction of nitro compounds in alkaline solution, the final production of hydrazo compound occurs essentially by reduction of the azo compounds and not of the azoxy compounds. Since azo compounds are only slowly reduced, only low current densities can be employed if a large useless evolution of hydrogen and waste of current are to be avoided; it is thus essential to reduce the strength of current to one half or still lower, as soon as the amount of electricity which is necessary for formation of the azo stage has been passed through the solution. Hydrazo compounds with the para-position to the two NH-groups unoccupied can be more or less easily transformed into isomeric benzidines.

4. Diamines and Amidophenols.

32. *p*-PHENYLENEDIAMINE FROM *p*-NITRANILINE.



Anode liquid: Sodium carbonate solution.

Cathode liquid: 20 gms. *p*-nitraniline, 5 gms. crystallized sodium acetate, 200 c.c. alcohol (70 %).

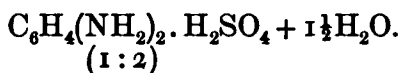
D_C : up to 20 amperes per 100 sq. cms. at the start, then decreasing down to 2 amperes; it is unnecessary but not

harmful to supply considerably more than the theoretical amount of current. After completion of the reduction, the hot cathode liquid is poured into a warm mixture of 50 c.c. concentrated sulphuric acid and 100 c.c. water, the *p*-phenylenediamine sulphate $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$, which has
(1:4)

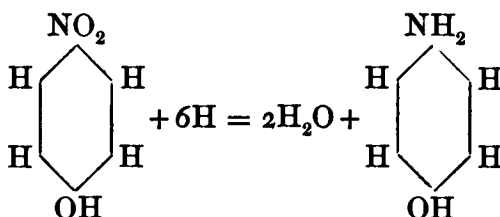
separated in almost colourless plates, is filtered off when cold, washed with water, and dried in the open air.

Current-efficiency over 90 per cent.; yield of material over 80 per cent. of the theoretical.

In similar manner and with the same yield *o*-phenylenediamine can be prepared from *o*-nitraniline in the form of a very well crystallized sulphate



33. *p*-AMIDOPHENOL FROM *p*-NITROPHENOL.



Anode liquid: Sodium carbonate solution.

Cathode liquid: 20 gms. *p*-nitrophenol and 6 gms. caustic soda are dissolved in 300 c.c. water by warming.

D_c : 10 amperes per 100 sq. cms., to be reduced towards the end to 2 amperes. Passage of current 10 per cent. more than that theoretically required. After completion of the reduction the cathode solution is made weakly acid by addition of moderately dilute sulphuric acid, and is then evaporated to dryness; the residue is extracted several times with a small amount of boiling alcohol and the combined extracts allowed to cool, when the sulphate of *p*-amidophenol crystallizes out in white needles. Current-efficiency 90 per cent.; yield of material 80 per cent.

Under the same conditions *o*-nitrophenol can be reduced to *o*-amidophenol; after the reduction, the cathode liquid is exactly neutralized with acetic acid and allowed to cool; a mixture of free amidophenol and its acetic acid salt separates in glistening plates, and is filtered off; the filtrate is extracted with ether, the ether distilled off, and the residue, with the first crop of crystals, re-crystallized from boiling water with the addition of a little animal charcoal. The *o*-amidophenol can be obtained quite pure by re-crystallization from benzene. Current-efficiency about 90 per cent.; yield of material over 60 per cent.

The reason why *p*-phenylenediamine can be obtained from *p*-nitraniline, whereas under the same conditions *m*-nitraniline compounds give azo compounds, lies, as previously explained, in the tendency of the *p*- and *o*-compounds to form quinone derivatives, which tendency is not possessed by the *m*-isomers. Since, during the whole progress of the reduction, no difficultly reducible substances are formed, the current density can be kept high and need only be diminished towards the end of the experiment, because then the cathode liquid contains scarcely any reducible material at all.

II. Electro-chemical Reduction of Carbonyl Compounds.

References: J. Tafel, *B.* 82, 3194-3206* (1899); 83, 2209-2224 (1900)*; *A.* 301, 302 (1899); *Z. ph. Ch.* 34, 187-228* (1900); J. Tafel and Baillie, *B.* 82, 68-77 (1899); J. Tafel and M. Stern, *B.* 30, 2224-2236 (1897); J. H. James, *Amer. Chem. Soc.* 21, 889-910 (1900); F. B. Ahrens and G. Meissner, *B.* 30, 532 (1897); E. Bandow and R. Wolfenstein, *B.* 81, 1577 (1898); H. Kauffmann, *Z. Elch.* 2, 365; 4, 461; K. Elbs, *Z. Elch.* 7, 644*; Chemische Fabrik auf Aktein, vorm. Schering, *D. R. P.* Nos. 95,623 and 96,362; E. Bandow and R. Wolfenstein, *D. R. P.* No. 94,949; E. Merck, *D. R. P.* Nos. 96,363 and 115,517; *D. R. P.* No. 113,719*; C. F. Boehringer und Söhne, *D. R. P.* No. 108,577*.

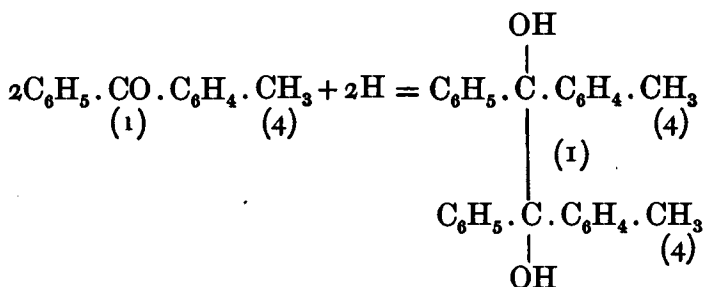
In opposition to the nitro compounds the carbonyl compounds belong in general to the class of difficultly reducible substances; their electrolytic reduction is best

carried out on a cathode of pure lead covered with a thin layer of spongy lead, which has a particularly high cathodic 'over-voltage.' This over-voltage is very strongly diminished by mere traces of impurity of foreign metals. Relative to this disturbing influence, the more usually employed heavy metals can be arranged in the following order: Pt, Ag, Sn, Hg, Zn, Fe; even traces of platinum exert an extraordinarily harmful action, whilst quite considerable amounts of iron, although making the action much slower, do not altogether prevent it. The satisfactory progress of the reaction is thus essentially dependent upon keeping all traces of foreign metals away from the cathode. The electrolyte, even that in the anode chamber, must contain no heavy metal other than lead; cathode and anode must be made of as pure lead as possible, and the current connexions so made that under no conditions can impurities from the brass connectors or copper wires reach the bath. The cathodes need a special preliminary treatment. They are first polished with wet sand, then electrolytically oxidized in 20 per cent. sulphuric acid (accumulator acid) with a current density of 2 amperes per 100 sq. cms. during half an hour, afterwards rinsed in cold water, immersed in boiling water for some minutes, washed with boiling alcohol, and dried quickly in a current of air. In this condition the cathodes can be preserved unaltered. With the exception of the polishing with sand this treatment is advantageously repeated after each experiment. The same treatment is suitable once even for the anodes, but does not need to be repeated; it is sufficient from time to time, after using, to soak them in water, wash them over, and quickly dry them. Foreign metals can easily be introduced by means of the porous pot; the new cells are therefore digested first with dilute caustic soda, then with water, and afterwards with hydrochloric acid of 1.02 to 1.03 sp. gr., each time for one to two days, and finally with water for a whole week. In the reduction of the carbonyl group we are concerned with three steps.

1. $2 >C=O + 2H = >\underset{\substack{| \\ >C.OH}}{C}.OH$
2. $>C=O + 2H = >CH.OH$
3. $>C=O + 4H = >CH_2 + H_2O$

1 and 2 are addition processes, 3 a splitting off of water with substitution of two hydrogen atoms for the oxygen atom. The same substance can undergo all three reduction stages according to the experimental conditions, but often one of these processes is the only one which occurs, and remains so even under varying conditions, or at any rate is the preponderating reaction. With ketones reactions 1 and 2 usually occur (formation of a pinacone 1, or a secondary alcohol 2); with acid amides, acid imides, and uric acid derivatives, however, 3 is the chief reaction. As high current-concentration as possible is in all cases to be desired.

34. PREPARATION OF PHENYL-*p*-TOLYLPINACONE FROM PHENYL-*p*-TOLYLKETONE.



Bath: Beaker with porous pot as anode chamber.

Anode liquid: 10 per cent. sulphuric acid.

Cathode liquid: 10 gms. phenyl-*p*-tolylketone, 180 c.c. alcohol (96 %), 20 c.c. sulphuric acid of 10 %.

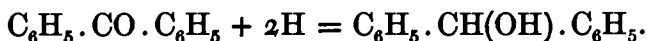
Anode: Lead plate.

Cathode: Perforated lead cylinder.

$D_c = 2$ amps. per 100 sq. cms. The bath is heated so that the cathode liquid is always gently boiling; at first

the evolution of hydrogen is small, but it becomes gradually stronger, and consequently, instead of the theoretical 1.4 ampere hours, 2 ampere hours are passed through the cell. The reduction should be complete in half an hour at the most; the boiling cathode liquid is filtered quickly, and the pinacone, which separates after cooling, is filtered off; the mother-liquor is concentrated by distillation to half its volume and in this way, after cooling, a further amount of pinacone is obtained. Both fractions are pure and melt at 164 degrees; yield of material 80 per cent.

35. BENZHYDROL FROM BENZOPHENONE.



Bath as in previous experiment, No. 34.

Anode liquid: Cold saturated sodium carbonate solution.

Cathode liquid: 30 gms. benzophenone, 500 c.c. alcohol (96 %), 100 c.c. water, 6 gms. crystallized sodium acetate.

$D_C = 0.4$ to 0.8 amperes per 100 sq. cms.

During the reduction, the alcoholic solution is kept nearly at the boiling-point; at first no hydrogen is evolved and the evolution only becomes strong quite towards the end of the experiment; instead of the theoretically required amount, 8.9 amp. hours, 9.5 to 10 amp. hours are passed through the cell. Duration of the experiment, four to six hours. The cathode liquid is afterwards neutralized with sulphuric acid, the alcohol is distilled off, and the oil which separates in the distilling flask is washed with water, after which it solidifies. The crystalline mass is filtered off, completely dried in a desiccator, and re-crystallized once from petroleum ether; it is thus obtained perfectly pure in snow-white needles of M.P. 67 to 80° C. Current-efficiency 80 to 90 per cent.; yield of material 90 per cent.

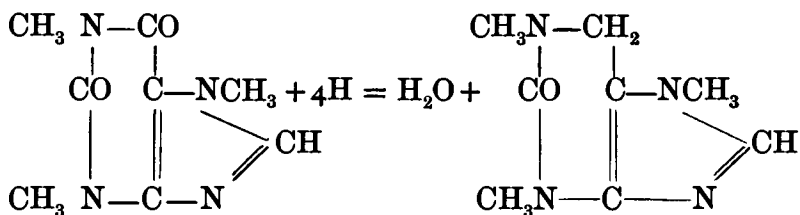
Reduced in moderately acid solution on lead electrodes, the purely aromatic ketones (i. e. such as have aromatic radicals to both sides of the carbonyl group) yield pinacones and small quantities of secondary alcohols; in

weak alkaline solution, however, they give very good yields of secondary alcohols. Fatty and fatty aromatic ketones (homologues of acetone and acetophenone) yield, in both cases, mixtures of pinacones and secondary alcohols, which can generally only be separated by a tedious process, when no special properties are of assistance, as, for instance, the excellent crystallization of pinaconehydrate,



Instructions for the preparation of benzophenone and phenyl-*p*-tolylketone are given in *J. pr.* **33**, 181; **35**, 465, 466.

36. DEOXYCAFFEINE FROM CAFFEINE.



Bath as in Nos. 34 and 35.

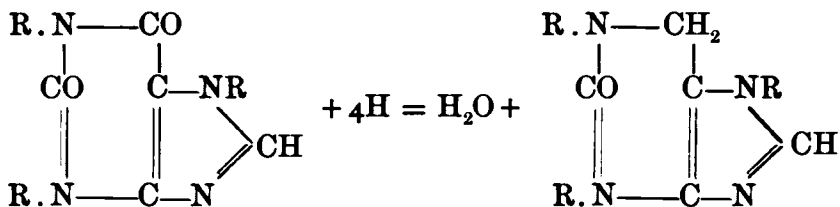
Anode liquid: 50 per cent. sulphuric acid.

Cathode liquid: 10 gms. caffeine, 25 gms. pure concentrated sulphuric acid, 25 gms. water.

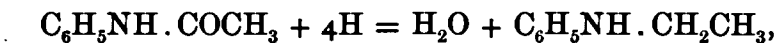
D_c : 2 to 4 amps. per 100 sq. cms. Passage of current about 6 amp. hours instead of the calculated 5 amp. hours; by external cooling with water, the temperature is prevented from rising above 18° C. During the whole progress of the experiment, a weak hydrogen evolution is observed. After the reduction is finished, the cathode liquid is neutralized with slaked lime, and the liquid filtered off from the precipitated gypsum, evaporated on the water-bath down to 30 or 40 c.c. and extracted with chloroform. After the evaporation of the chloroform, a yellow crystalline mass remains, which is dissolved in 10 per cent. hydrochloric acid and the solution extracted with chloroform for the removal of caffeine. (Caffeine is a weaker base than deoxy-

caffeine.) The aqueous solution is now made alkaline and the deoxycaffeine extracted from it by chloroform; it crystallizes out in colourless needles on evaporation of the solvent. The crystals obtained in this way contain one molecule of water of crystallization and melt at 118°C .; over sulphuric acid they give up their water of crystallization and then melt at 148° . If the evaporation of the filtrate from the gypsum precipitate be neglected, the extraction is more tedious, but the yield is somewhat higher and the deoxycaffeine crystallizes more easily. Current-efficiency 75 to 80 per cent.; yield of material about 70 per cent. of the theoretical.

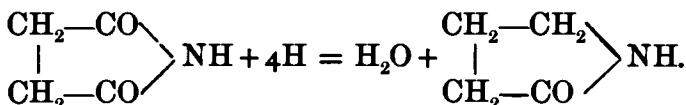
The reduction of caffeine to deoxycaffeine is a single case of a general method; under similar experimental conditions, theobromine and other alkyl xanthines can be reduced to dihydroxypurines.



In the same way the method is suitable for the reduction of many ordinary acid amides and imides; thus ethylaniline is formed from acetanilide:

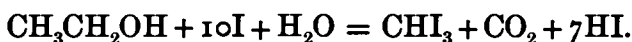


and pyrrolidone from succinimide:



C. ELECTRO-CHEMICAL OXIDATION METHODS.

37. PREPARATION OF IODOFORM.



References: K. Elbs and A. Herz, *Z. Elch.* 4, 113-118*; E. Foerster and

W. Mewes, *Z. Elch.* 4, 268-272*; Chemische Fabrik auf Aktien, vorm. Schering, D. R. P. No. 29,771.

A beaker contains a large anode of platinum wire-gauze or sheet and a small cathode of platinum foil wrapped in parchment paper.

Electrolyte: 20 gms. anhydrous sodium carbonate, 20 gms. potassium iodide, 200 c.c. water, 50 c.c. alcohol (96 %).

$D_A = 1$ to 3 amps. per 100 sq. cms.; $D_C = 4$ to 8 amps. During the experiment the electrolyte is warmed to 50-70°C. and a current of CO_2 passed through the solution between the anode and cathode; in this way an approximate neutralization of the free alkali produced at the cathode and a satisfactory stirring are effected.

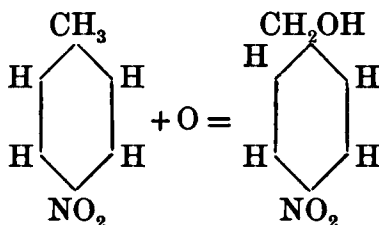
The correct amount of the current of carbonic acid is determined by observing that the solution becomes light to dark yellow in colour; if it should become brown from the separation of free iodine, the current of CO_2 should be interrupted for a time.

The iodoform which separates in the crystalline state is filtered off after cooling; it is washed with water and dried at the temperature of the room; the filtrate, after addition of fresh quantities of potassium iodide and alcohol, can be used over again several times for the production of further amounts of iodoform, until it contains very large quantities of potassium carbonate and iodate. Current-efficiency about 80 per cent. The above equation represents the formation of iodoform, neglecting the intermediate products and secondary reactions.

The hydriodic acid reacts, of course, with the sodium carbonate present to give sodium iodide and carbonic acid; the sodium iodide is continually decomposed by the current, making fresh quantities of iodine available at the anode. The iodine produced at the anode, coming in contact with the free alkali or alkali carbonate from the cathode, forms with it hypoiodite both as alkali salt and as free acid; this reacts with the alcohol by simultaneous oxidation and iodizing to produce iodoform and carbonic acid. The chief

by-product is alkali iodate, which is produced from that portion of the hypoiodite which does not immediately react with the alcohol.

38. *p*-NITROBENZYLALCOHOL FROM *p*-NITROTOLUENE.



Reference : K. Elbs, *Z. Elch.* 2, 522-523*.

A cylinder of lead placed in a beaker forms the cathode ; a porous pot serving as the anode chamber contains as large an anode as possible of platinum foil or, better, platinum gauze.

Cathode liquid : Sulphuric acid of 1.6 to 1.7 sp. gr.

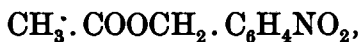
Anode liquid : 15 gms. *p*-nitrotoluene, dissolved in 80 gms. glacial acetic acid mixed with 15 gms. concentrated sulphuric acid and 7 gms. water.

D_A : at most 1.5 amps. per 100 sq. cms.

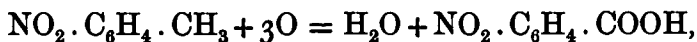
D_C : unimportant.

During the experiment the apparatus is kept in a bath of boiling water ; the efficiency of the anode action, despite the low current density, is low ; oxygen escapes all the time, and three times as much electricity must be passed as the theoretical. Scarcely any hydrogen escapes at the cathode since it is used up in reducing the sulphuric acid to sulphur. The dark brown anode liquid is distilled with steam, when besides acetic acid, the unaltered *p*-nitrotoluene passes over, as also some *p*-nitrobenzyl alcohol, the recovery of which is, however, scarcely profitable. The contents of the distilling flask are filtered through a double filter-paper, the residual resinous material is extracted twice with boiling water and the solution added to the original

filtrate; upon cooling, raw *p*-nitrobenzylalcohol crystallizes in long, yellowish-brown needles. From the mother-liquor, besides *p*-nitrobenzylalcohol and some *p*-nitrobenzylacetic ester,



a small amount of a difficultly soluble substance—the ether of *p*-nitrobenzylalcohol, $\text{NO}_2\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2$, is extracted by shaking with ether. By boiling the residue obtained by distilling off the ether, with a little alcohol, only the *p*-nitrobenzylalcohol and its acetic ester are dissolved. The purification of the whole amount of the raw product is best carried out by re-crystallization from boiling water with the addition of some animal charcoal. As an average, a 40 per cent. yield of *p*-nitrobenzylalcohol is obtained, calculated from the nitrotoluene; the current-efficiency being 30 per cent. The formation of *p*-nitrobenzyl alcohol by anodic oxidation is remarkable, since the first oxidation step is obtained as final product, whilst all other oxidizing agents produce *p*-nitrobenzoic acid,



which is the third oxidation step.

APPENDIX

TABLE OF ELECTRO-CHEMICAL EQUIVALENTS

Element.	Symbol.	Valency.	Atomic Weight.	Electro-chemical Equivalent in grams for 1 ampere hour.
Aluminium . .	Al	3	27·11	0·338
Antimony . .	Sb	3	119·9	1·494
Arsenic . . .	As	3	75·1	0·936
Bismuth . . .	Bi	3	208·9	2·597
Bromine . . .	Br	1	79·96	2·984
Cadmium . . .	Cd	2	112·0	2·087
Calcium . . .	Ca	2	40·01	0·746
Carbon	C	4	12·0	0·112
Chlorine . . .	Cl	1	35·46	1·322
Chromium . .	Cr	2	52·14	0·982
		3		0·655
Cobalt	Co	2	59·6	1·097
		3		0·732
Copper	Cu	1	63·60	2·362
		2		1·184
Fluorine . . .	F	1	19·1	0·716
Gold	Au	1	197·2	7·356
		3		2·452
Hydrogen . . .	H	1	1·008	0·0373
Iodine	I	1	126·86	4·747
Iron	Fe	2	56·02	1·045
		3		0·696
Lead	Pb	2	206·91	3·852
Lithium	Li	1	7·03	0·263
Magnesium . .	Mg	2	24·36	0·454
Manganese . . .	Mn	2	54·94	1·022
Mercury	Hg	1	200·3	7·470
		2		3·735
Nickel	Ni	2	58·9	1·094
Nitrogen	N	3	14·04	0·175
Oxygen	O	2	16·00	0·299
Phosphorus . .	P	3	31·03	0·387
Platinum . . .	Pt	4	194·8	1·814
Potassium . . .	K	1	39·12	1·459
Silicon	Si	4	28·38	0·265
Silver	Ag	1	107·92	4·025
Sodium	Na	1	23·05	0·860
Sulphur	S	2	32·06	0·598
Tin	Sn	2	119·10	2·224
		4		1·112
Zinc	Zn	2	65·41	1·220

INDEX

- Acetanilide, 94.
Acid amides, 94.
— imides, 94.
Acrylic acid, ethyl ester of, 58.
Adipic acid, ethyl ester of, 56.
Amidodiphenylamine, 67.
Amidophenols, 61, 65, 69, 87, 88.
Amidophenol sulphonic acid, 71.
Ammeter, 4.
Ammonium persulphate, 35.
Ampere-hour meter, 4, 7.
Ampere manometer, 5.
Aniline, 58, 68.
Anodes, 11.
Azobenzene, 63, 78.
Azobenzoic acid, 79.
Azotoluene, 78.
Azoxyanisol, 76.
Azoxybenzene, 63, 76.
Azo-xylene, 74, 79.
Azoxy-xylene, 74.

Barium hypochlorite, 25.
— perchlorate, 34.
Benzhydrol, 92.
Benzidine, 69, 82.
— disulphonic acid, 85.
— sulphate, 83.
Benzophenone, 92.
Benzoylazoxydiphenylamine, 67.
Benzylidene-phenylhydroxylamine, 72.
Bleaching solutions, 25.
Brass, preparation of copper from, 45.
Bromates, 28.
Butane, 54.

Cadmium oxide, 41.
Caffeine, reduction of, 93.
Carbon electrodes, 11.
Carbonyl compounds, reduction of, 89.
Cathodes, 11.
— lead, 90.
Cells, electrolytic, 10.
— porous, 14.
Chlorates, 25.

Chlornitrobenzene, 75.
Chromate, lead, 42.
Chromate, use of, in preparation of chlorates, 26, 27.
— use of, in preparation of hypochlorites, 22, 24.
Chrome alum, 17.
Chromic acid, 17.
Chromium sulphate, 17.
Copper carbonate, basic, 42.
— connexions, 1.
— electrodes, 11.
— phosphate, 42.
— preparation of, from brass, 45.
— voltameter, 6.
Cupric oxide, 40.
Cuprous oxide, 40.
Current concentration, 10.
— density, 9.

Deoxycaffeine, 93.
Diamidoazobenzene, 64, 80.
Diamidoazoxybenzene, 80.
Diamidobenzidine, 83.
Diamidohydrazobenzene, 83.
Diamido-oxyazobenzene, 81.
Diamines, 87.
Diaphragms, 14, 15.
Dichlorazoxybenzene, 75.
Dihydroxypurines, 94.

Electrode, potential, 9.
Electrodes, 11.
Electrolysis apparatus, 10.
Electrolytic cells, 10.
Equivalents, electro-chemical, 98.
Ethane, 51.
Ethylaniline, 94.
Ethylene, 53.
— dibromide, 53.

Ferrous oxide, 41.

Gas analysis methods, 22.

Hydrated basic salts, 42.
— metallic oxides, 41.
Hydrazobenzene, 60, 78, 82.

- Hydrazo compounds, 82.
 Hydrazotoluene, 83.
 Hypobromites, 31.
 Hypochlorites, 21.
 Hypiodites, 31.
 Iodates, 29.
 Iodoform, 95.
 Iron electrodes, 11.
 — oxide, 41.
 Ketones, reduction of, 89.
 Lead, basic carbonate of, 41.
 — cathodes, preparation of, 90.
 — chromate, 42.
 — disulphate, 42.
 — electrodes, 11, 90.
 Measurements, electrical, 4.
 Measuring instruments, 4.
 Nickel electrodes, 11.
 Nickeline wire, 3.
 Nitraniline, 64, 80, 83.
 Nitroanisol, 65, 76.
 Nitrobenzene, 58, 68, 71, 72, 76, 78, 82.
 Nitrobenzenesulphonic acid, 85, 86.
 Nitrobenzoic acid, 79.
 Nitrobenzoyldiphenylamine, 67.
 Nitrobenzylacetic ester, 97.
 Nitrobenzyl alcohol, 96.
 Nitro compounds, reduction of, 57, 60, 61, 63.
 Nitrodiphenylamine, 67.
 Nitrophenols, 65, 88.
 Nitrosobenzene, 58.
 Nitrotoluene, 68, 78, 96.
 Nitrotoluenesulphonic acid, 86, 87.
 Nitroxylene, 74, 79.
 Organic acids, electrolyses of, 47.
 Over-voltage, 90.
 Oxidation of chromium sulphate, 17.
 — copper, 40.
 — organic compounds, 94.
 Perbromates, 35.
 Perchlorates, 33-35.
 Periodates, 35.
 Persulphates, 35-40.
 Phenylenediamines, 64, 87.
 Phenylenediamine sulphates, 88.
 Phenylhydroxylamine, 58, 72.
 Phenyltolylketone, 91, 93.
 Phenyltolylpinacone, 91.
 Pinaconehydrate, 93.
 Platinum electrodes, 11, 12.
 Plumbic sulphate, 42.
 Polarization, 8.
 — current, 8.
 Pole reagent paper, 3.
 Potassium bromate, 28.
 — chlorate, 26.
 — iodate, 29.
 — perchlorate, 33.
 — persulphate, 38.
 Potential difference, 8.
 Propionate, sodium, 53.
 Pyrrolidone, 94.
 Quinone diimide, 64.
 — imidoxime, 65.
 Resistances, 3.
 Sodium bromate, 28.
 — chlorate, 27.
 — hypochlorite, 21.
 — iodate, 29.
 — perchlorate, 34.
 — trichloracetate, 54.
 Stirring, 10.
 Succinic acid, 56.
 Succinimide, 94.
 Theobromine, 94.
 Tolidinedisulphonic acid, 86.
 Tolidine sulphate, 83.
 Trichloracetic acid, trichloromethyl ester, 54.
 Voltameters, copper, 6.
 — water, 5.
 Voltmeters, 8.
 Water voltameter, 5.
 White lead, 41.
 Xanthines, 94.
 Zinc oxide, hydrated, 42.

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